THE ANALYSIS OF DRUGS AND CHEMICALS.

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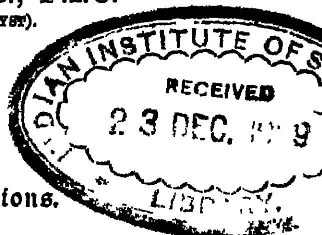
THE ANALYSIS OF DRUGS AND CHEMICALS

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DEDICATED TO OUR FORMER CHIEF,

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PREFACE.

In the past, the Analysis of Drugs has generally been treated in English text-books as an adjunct to Food Analysis, usually from the point of view of the Foods and Drugs Acts, and in a more or less incomplete manner. The analysis of Pharmaceutical Materials has also been treated in such works as Squire's *Companion to the British Pharmacopœia*, but chiefly from the point of view of the official requirements for drugs.

We have, therefore, undertaken this work in the hope that a book dealing with the analysis of drugs and chemicals from the analyst's point of view, in a more complete manner than hitherto, will prove useful to all those who are brought into contact with these materials, whether as works' chemists or in a public or consulting capacity. We hope that the association of the points of view, and of the experience, of a Public Analyst and a Pharmaceutical Works' Chemist in this work will add to its completeness and value.

An endeavour has been made to include methods for the examination of practically all substances likely to be met with in practice, and for which methods of analysis are available. Where no such methods are available, the drugs have been omitted, however important they may be in other respects. In some cases new processes, or modifications of old processes, have been worked out for this purpose. Only well-tried methods, or methods of which we have had personal experience, have been included.

In order to keep the volume to a size suitable for a laboratory handbook, the descriptions have purposely been made as concise as possible. It is hoped that sufficient detail has been supplied in each case to enable a trained worker to follow the descriptions with ease, but the style naturally has suffered somewhat. It is hoped, however, that the advantage of smaller size will outweigh any possible disadvantage of style due to brevity.

In the preparation of this volume we have made use of most of the standard works on the various subjects treated, and general acknowledgment is here made. Particular acknowledgment is made throughout the book where such is necessary.

Our thanks are due to Mr J. R. Stubbs for two drawings, for reading the whole of the proofs, and for helpful suggestions; to Messrs Baird, Tatlock and Co., Ltd., A. Gallenkamp & Co., Ltd., and Adam Hilger, Ltd., for the loan of blocks for illustrations.

N. E.
G. D. E.

March 1929.



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ANALYSIS OF DRUGS AND CHEMICALS.

PART I.

INTRODUCTION.

THE analysis of drugs and chemicals requires, apart from the apparatu usual in a chemical laboratory, the following special instruments : Micrc scope, polarimeter, refractometer, a Westphal balance, and a Lovibond tinto meter. Apparatus for the colorimetric and electrometric determinatio of hydrogen-ion concentration and for electrometric titration is essential In fitting up a laboratory for the purpose, it is essential that a good suppl of the following should be provided :—

Accurately graduated specific gravity bottles and volumetric apparatus

Separating funnels (pear-shaped), arranged in batteries on woode stands.

Fat-extraction apparatus.

Reflux condensers for saponification or acetylation.

Stills for the recovery of volatile solvents.

Stills for alcohol determinations (see fig. 19).

Weighed flat-bottomed dishes of metal or glass for total solid determinations.

Weighed Gooch crucibles or Soxhlet tubes for insoluble matter, etc.

Small weighed flasks for alkaloids, oils, etc.

As a description of the microscopic character of drugs is outside the scope of this book, the reader is referred to any of the numerous works on this subject for details of the construction of the microscope. It may not, however, be out of place here to say that the authors use a microscope fitted with $\frac{2}{3}$-in. and $\frac{1}{6}$-in. objectives, 2 and 4 (continental) eyepieces, a sub-stage condenser, a mechanical stage, and a polariscope. A list of books suitable for use in connection with the microscopical analysis of drugs will be found in the Appendix.

The more uncommon instruments will be described from the point of view of their applications to drug analysis. No attempt will, however, be made to describe the principles on which they are based.

CALIBRATION OF APPARATUS.

Under this heading will be found brief directions for the calibration of pipettes, burettes, and measuring flasks; the calibration of thermometers is dealt with on p. 9. Before any attempt is made to calibrate glass apparatus it must be thoroughly cleaned and dried. The best method of cleaning glass is to fill the vessel with hot concentrated sulphuric acid to

which a quantity of powdered potassium bichromate has been added, and allow it to stand for a few minutes. The apparatus is then rinsed several times with distilled water. For the most accurate work it is essential that glass measuring instruments be kept scrupulously clean, and to this end they should be treated from time to time with the above chromate mixture.

In the past, volumetric apparatus was frequently standardised on the basis of Mohr's litre, which was the volume of 1000 gm. of water weighed in air at 15·5° or 17·5° C. with brass weights. This method has now been given up almost entirely, and the basis of calibration is the volume of 1000 gm. of water at 4° C., the weight being reduced to vacuum. A 1000th part of this, which is almost but not quite equal to the true cubic centimetre (1 litre equals 1000·027 cc.) is now taken as the standard, and it has been suggested that this be described as the *millilitre* (ml.). This suggestion has been made in the report of the Joint Committee for the Standardisation of Scientific Glassware, obtainable from the Secretary of the Committee at the Institute of Chemistry. An abstract of the report has been prepared.[1] For those workers who prefer to use Mohr's system it may be taken that 1000 Mohr cc. (described as "1000 G.W.A.") equals 1002 ml.

Calibration of Measuring Flasks.—The perfectly clean and dry flask is placed on the right-hand pan of a balance together with standard weights slightly in excess of the nominal capacity of the flask. A similar flask is placed on the left-hand pan of the balance and weights are added until equilibrium is obtained. The flask and weights are now removed from the right-hand pan and the flask filled with water at room temperature until the bottom of the meniscus just reaches the mark on the neck, care being taken that no water is left in drops on the neck above the mark. The flask is now placed on the right-hand pan of the balance and standard weights added until equilibrium is again obtained. The difference between this and the previous weight obtained gives the actual weight of water contained in the flask. The temperature of the water is now taken and the weight obtained is corrected by adding the number of milligrams given in Table I., corresponding to the temperature of the water. This table is constructed for a 1000 cc. flask; for smaller or larger flasks the corresponding fraction or multiple of the correction should be used.

Correction for barometric pressure and temperature of the air may be also made, but for ordinary purposes this is not necessary.

Should the weight differ materially from the capacity of the flask, water should be added or removed until the correct weight is obtained and the neck of the flask marked at this point. A method of marking is suggested on p. 4.

Calibration of Pipettes.—For the most accurate work, pipettes (which are by far the most accurate of the ordinary instruments used in volumetric analysis) should have a narrow upper stem, and should not deliver too rapidly; 25 to 30 seconds is a satisfactory time for a 20-cc. pipette, and others in proportion. They should, of course, be absolutely clean. Compare the Report of the Committee[2] and the pamphlet published by the Metrology Department of the National Physical Laboratory.

The pipette is filled to the mark with distilled water of known temperature, and this is then allowed to flow into a tared flask. The flask is again

[1] *Analyst*, 1924, **49**, 479.
[2] *J. Soc. Chem. Ind.*, 1919, **38**, 280 R.

weighed and the weight of water delivered is corrected for temperature from Table I below. If the weight of water so delivered is not correct, a mark is made on the stem with ink (or a label is gummed on) about 3 cm. from the first mark, and the amount delivered from this mark found. Having thus found two marks, the volume delivered from each of which is known, and also the distance between them, it is easy to calculate the point at which the pipette will deliver the correct volume. This point is marked temporarily and the pipette again tested. If the point is found to be the correct one it is marked permanently with a file, or better as described below.

TABLE I.

THE NUMBER OF MILLIGRAMS TO BE ADDED TO THE OBSERVED WEIGHT OF WATER IN A LITRE FLASK ACCORDING TO THE TEMPERATURE OF THE WATER.

Temperature ° C.	0·0	0·2	0·4	0·6	0·8
10	1502	1515	1528	1542	1556
11	1571	1587	1603	1619	1636
12	1654	1672	1690	1709	1729
13	1749	1769	1790	1811	1833
14	1855	1878	1901	1925	1949
15	1974	1999	2025	2051	2077
16	2104	2132	2160	2188	2217
17	2246	2276	2306	2336	2367
18	2399	2430	2463	2496	2529
19	2562	2596	2631	2666	2701
20	2737	2773	2810	2847	2884

Calibration of Burettes.—Cheap burettes should not be used, neither should those be used having a rubber connection; one of the easiest burettes to work with is the Schellbach form with glass tap, although these are not recommended for the most accurate work. All burettes should deliver slowly and should, as a general rule, not be used for delivering large volumes; for volumes of more than 10 cc. (for accurate work), pipettes should be used as far as possible. In titration, where the most accurate results are desired, it is better to add the bulk of the liquid from a pipette and the remainder, not more than 5 cc., from a delicate burette.

The total volume of the burette is determined by filling it up to the zero mark with distilled water and then allowing it to empty slowly into a tared flask. The uniformity of the graduations is tested by running off portions of 2 to 5 cc. at a time and weighing each portion before the addition of the next. If the errors in a burette are at all serious it should be rejected, as it is quite possible to obtain instruments which give results very near to the truth. The National Physical Laboratory recommends that the graduation marks be carried at least halfway round the tube, and that at least every tenth line should be carried completely round and numbered.

The Marking of Volumetric Apparatus.—Although this may be done with a file the method is not very satisfactory, especially in the case of pipettes (on account of the risk of fracture), and the method given below is much better. A strip of gummed paper having a straight edge is fitted round the stem of the instrument to be marked, and placed accurately in position so that the edge of the paper occupies the line where the mark is to be placed; the stem is then coated with a thin layer of hard paraffin for some distance on either side of the paper. When the paraffin has hardened, a ring is cut with a knife along the edge of the gummed paper and the exposed glass is then etched with hydrofluoric acid rubbed in with a pad of cotton-wool attached to a piece of copper wire.

THE DETERMINATION OF SPECIFIC GRAVITY.

The specific gravity (S.G.) or density of a liquid may be determined in several ways; by a hydrometer, by the Westphal balance, by a specific gravity bottle, or by the Sprengel tube, the last being the method which is, under certain circumstances, susceptible of the greatest accuracy.

With the exception of certain substances, such as fats, it is now usual to take specific gravities at 15·5° C. (60° F.) compared with water at the same temperature. When, for some reason, another temperature is used, it is usual to state this by employing a fraction, the numerator of which expresses the temperature of the determination and the denominator that of the standard volume of water. Thus, to say that the specific gravity of a liquid is 1·3742, $\frac{15·5°}{4°}$ means that its weight at 15·5° C. is 1·3742 compared with the weight of an equal volume of water at 4° C. The standard temperatures usually adopted in analysis are $\frac{15·5°}{15·5°}$.

The Hydrometer.—The ordinary hydrometer is made of glass, and consists of a stem carrying a scale on which the specific gravity is read, a cylindrical body, and a lower bulb containing mercury in order to cause the whole to float upright. The liquid to be tested is contained in a small cylinder sufficiently wide to take the hydrometer comfortably. The instrument is put in, making sure that there are no adherent air bubbles and that the stem is wet with the liquid for a short distance above the level of the liquid. For transparent liquids it is better to take the reading by looking under the surface, having the eye on a level with the surface, and taking the point where this appears to cut the hydrometer as the true reading.

Hydrometers carefully made and standardised and reading over a short range are capable of considerable accuracy. Thus, one reading between 0·930 and 0·960 has been used by the authors for some considerable time for approximate determinations of alcohol in spirits, and has frequently been tested against the specific gravity bottle, the two methods rarely giving results differing by more than three in the fourth decimal place.[1]

The Westphal Balance.—An ordinary form of the Westphal balance is shown in fig. 1, which, to a large extent, explains itself. It is a balance on the steelyard principle, at one end of which hangs a plummet which dis-

[1] Standard hydrometers for mineral oils have been designed by the Institution of Petroleum Technologists. With suitable corrections they may be used for other substances.

places exactly 5 cc. of water. When the plummet hangs in air, the balance is adjusted so that the two points are exactly opposite one another. When the plummet is immersed in some liquid, riders have to be added to bring the balance again into equilibrium. The largest rider weighs 5 gm. (for a 5 cc. plummet), so that the first decimal place is shown by the position of this on the beam when the system is in equilibrium; other riders are used, being one-tenth, one-hundredth, and one-thousandth of this—these, there fore, show the second, third, and fourth decimal places respectively. For liquids denser than water, one of the largest riders is hung from the plummet

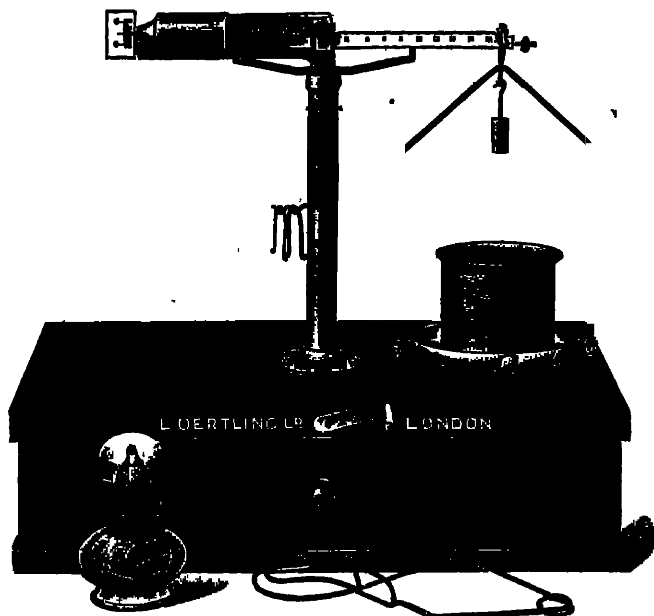


FIG. 1.—Westphal Balance.

hook. Should it happen that two riders occupy the same notch on the beam, the smaller is hung from the larger.

The Westphal plummet can be used in connection with an ordinary balance, which is, of course, more delicate than the Westphal balance. The jar holding the liquid to be tested is placed on a fixed support striding the balance pan, and so arranged that the latter can move freely without coming in contact with it. The method is capable of considerable accuracy.

The Specific Gravity Bottle.—There are various types of specific gravity bottles, some being shown in fig. 2. The most accurate form is probably the one having a thermometer and side tube. For ordinary purposes, a bottle holding 25 cc. or 50 cc. is the most convenient size, but bottles holding 10 cc. and 100 cc. are commonly used. Before use the bottle is carefully cleaned, dried, and weighed. It is then filled with distilled water at a temperature lower than that of the room and the thermometer stopper inserted (these directions refer to the bottle having a thermometer stopper and side tube), the thermometer having been previously standardised against an instrument

known to be correct. The outside of the bottle is carefully dried and the bottle allowed to stand for some time at room temperature, the liquid exuding from the capillary tube being removed with a soft duster. When the temperature has become constant the reading is carefully noted, the capillary tube finally wiped, and the cap adjusted. The bottle is then carefully weighed, the total weight, less the weight of the bottle, giving the capacity of the bottle at the particular temperature used. If the temperature is not exactly 15·5° C. the weight can easily be corrected to this temperature from



FIG. 2.—Specific Gravity Bottles.

the Table on p. 7. Repeat determinations at the same temperature should not differ by more than 1 mg. for a 100 cc. bottle, and others in proportion. When determining the specific gravity of some other liquid the bottle is filled with that liquid, exactly as described above, and the specific gravity calculated in the usual manner.

The Sprengel Tube.—The Sprengel tube is susceptible of a higher degree of accuracy than any other method of taking specific gravity; it is particularly useful when only small quantities of liquid are available. It consists essentially of a U-tube, the ends of which are drawn out to a capillary and bent at right angles. One of the capillary tubes is drawn out to a point and the other has a mark on it. For use the whole is filled with the liquid and immersed in a bath of water at 15·5° C. When no further expansion or contraction takes place the liquid is carefully adjusted on the mark by applying a piece of filter paper to the pointed end; it is then wiped and weighed. The Ostwald modification of the Sprengel tube is shown in fig. 3.

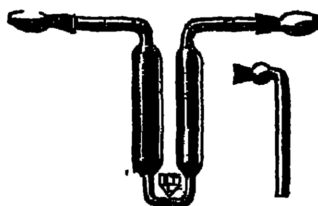


FIG. 3.—Sprengel Tube.

The Specific Gravity of Solids.—When the solid is in powder form the specific gravity bottle may be used. A quantity of the solid is added to the bottle and the whole weighed; if the weight of the bottle is w_1 and the total weight w, the weight of the added solid is given by $w-w_1$. The bottle is then completely filled (great care is here necessary to avoid air bubbles) with a liquid of known specific gravity d, in which the solid is insoluble, and the weight is again taken$=w_2$. Let w_3 be the weight of the

bottle filled with water, then the specific gravity D of the solid is given by

$$D=\frac{(w-w_1)d}{(w_3-w_1)-(w_2-w)}.$$

If the solid is in lump form its specific gravity may be determined by finding its weight in air and its apparent weight when immersed in a liquid of density d; the specific gravity, D, of the solid is given by

$$D=\frac{wd}{w-w_1}.$$

The specific gravity of solids lighter than water, such as waxes, may be taken by this second method by attaching to the substance another solid (say a piece of lead) which is sufficiently heavy to submerge the lighter body in the liquid which is being used. Using the above notation, if s is the weight of the sinker in the liquid, and w_2 the apparent weight of the sinker and the substance in the liquid, then the specific gravity of the substance is given by—

$$D=\frac{wd}{w-(w_2-s)}.$$

In taking the specific gravities of waxes it is very important to see that the substance is free from air bubbles. The best method of getting rid of these is to melt the wax and cool thoroughly in a vacuum desiccator for some hours.

TABLE II.

SHOWING THE SPECIFIC GRAVITY OF WATER AT DIFFERENT TEMPERATURES.

Temperature °C.	Specific Gravity. Unity at 15·5° C.	Temperature °C.	Specific Gravity. Unity at 15·5° C.
9	1·000757	15·5	1·000000
10	1·000676	16	0·999920
11	1·000582	17	0·999752
12	1·000475	18	0·999572
13	1·000354	19	0·999381
14	1·000221	20	0·999179
15	1·000076	21	0·998967

DETERMINATION OF THE MELTING-POINT.

The usual method of taking the melting-point of substances fusing below 200° to 300° C. is to place a small quantity in a thin glass capillary tube (made by softening a piece of ordinary glass tubing about 5 mm. in width in the flame, and drawing it out) closed at one end. The tube is attached to the bulb of a thermometer by a small rubber band (this is easily made by cutting about $\frac{1}{16}$ in. from a piece of ordinary $\frac{3}{16}$ in. rubber tubing), so arranged that the substance is at the middle point of the bulb. The thermometer is then placed in some suitable liquid bath provided with a stirrer, which is gently heated by means of a very small flame.

The best liquid for the bath is medicinal liquid paraffin. For temperatures much above 200° C. a solid paraffin bath may be used, or, if preferred, sulphuric acid mixed with varying proportions of potassium sulphate. An apparatus provided with electrical heating arranged for the determination is shown in fig. 4.

The melting-point thus obtained may be written as M.Pt.$=x°$ C. (uncorr.), or a correction may be applied to allow for that portion of the mercury thread which is not immersed in the bath; in this case the true melting-point is written M.Pt.$=(x+x')°$ C. (corr.). The method for obtaining this correction will be found on p. 9, x' being the correction applied.

Another method which is sometimes used for taking melting-points,

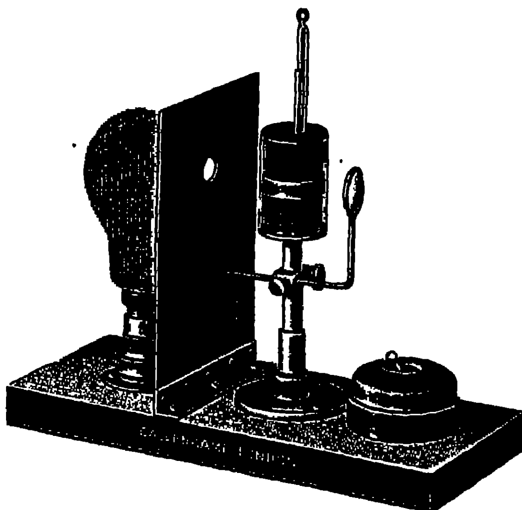


FIG. 4.—Melting-point Apparatus.

when a larger amount of substance is available, consists in melting about 15 to 20 gm. in a test-tube, placing a thermometer in the liquid and taking readings from time to time as the liquid cools, say every half-minute, with constant stirring. The temperature will gradually fall until a point is reached at which it will remain constant for several minutes, or even rise slightly. The constant temperature or the highest temperature reached during the rise is taken as the melting-point of the substance. Strictly speaking this point is, of course, the solidifying point, but in general (where super-cooling is avoided) this will have the same value as the melting-point. It will need to be corrected for that portion of the mercury column not immersed (p. 9). The melting-points of fats are difficult to determine, and cannot be obtained with much accuracy by either of these methods. The subject is further discussed in Part VI of this book.

DETERMINATION OF THE BOILING-POINT.

To determine the boiling-point of a substance, about 25 gm. or more are placed in a small distilling flask together with a few small pieces of porous pot (unglazed porcelain). The neck is closed with a cork through which is

passed a thermometer so arranged that the whole of the column of mercury will be surrounded by the vapour of the boiling liquid. The flask is heated by a small direct flame as uniformly as possible, and in such a manner that it is not heated above the level of the liquid. A small condenser may be attached to the side tube. When, as in the case with liquids having high boiling-points, it is not possible to have the whole of the mercury column surrounded by liquid, a correction must be applied as described below. When there is any doubt as to the purity of some particular substance it should be distilled completely and the range of temperature noted—a pure substance will distil completely at one temperature, if no decomposition takes place.

Unfortunately the above method cannot be applied when only a small quantity of material is available, but a method has been suggested by Schleirmacher[1] which requires a few drops only, but which, however, is only applicable to those substances which do not react with mercury and whose boiling-points are under 220° to 230° C., the temperature at which the vapour pressure of mercury ceases to be negligible. The method consists of heating the liquid in the closed limb of a U-tube, the remainder of the limb being filled with mercury, in a water or paraffin bath containing a thermometer. The temperature is taken at that point at which the mercury is at the same level in each limb. This temperature is that which the vapour pressure of the substance is equal to the pressure of the atmosphere, *i.e.* the boiling-point of the substance.

Another method which may be used with advantage is as follows: A short piece of tubing, about 7 to 10 mm. wide and 3 cm. long, closed at one end, is about two-thirds filled with the liquid, and a piece of capillary tube closed at one end is placed in it with the open end downwards. The whole is then attached by a rubber band to a thermometer, inserted in a test-tube, and heated in a suitable bath. On warming up, a few air bubbles slowly escape from the bottom of the capillary tube, but when the boiling-point is reached the succession of bubbles becomes rapid and continuous.

Correction of Melting- and Boiling-Points.—If in the determination of melting-points or boiling-points the whole of the thread of mercury is not immersed in the hot liquid or vapour, the temperature as read will not give the correct melting-point or boiling-point, but will be too low. This can be corrected by means of the following equation :—

$$t(\text{corr.}) = t + 0{\cdot}000156 \times l \times (t - t').$$

Where t is the temperature read off on the thermometer, t' is the temperature of the thread, of length l in scale degrees, which is not in the liquid or vapour, and 0·000156 is the coefficient of expansion of mercury in glass. The correction may amount to as much as two degrees or even more, so that it should never be neglected. All melting-points given in this book are corrected, except in those instances where the contrary is definitely stated.

Standardisation of Thermometers.—Whenever possible, it is desirable to use thermometers which have been standardised at the National Physical Laboratory, or, from motives of economy, thermometers which have been compared with these. Where this is not possible the upper portions of a thermometer may be tested by taking the boiling-point of certain pure substances and comparing the readings obtained with the true boiling-

[1] *Ber.*, 1891, **24**, 944.

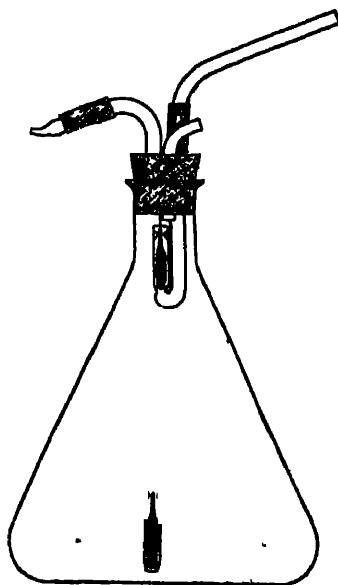
points. The boiling-points for water, naphthalene, and benzophenone are given in the following table :—

TABLE III.

Pressure in mm. Hg.	Water. B.Pt. °C.	Naphthalene. B.Pt. °C.	Benzophenone. B.Pt. °C.
720	98·5	215·7	303·5
725	98·7	216·0	303·8
730	98·9	216·3	304·2
735	99·1	216·6	304·5
740	99·3	216·9	304·8
745	99·4	217·2	305·2
750	99·6	217·5	305·5
755	99·8	217·8	305·8
760	100·0	218·1	306·1
765	100·2	218·4	306·4
770	100·4	218·7	306·7

DETERMINATION OF SOLUBILITY.

An important point in connection with the purity of a chemical is that its solubility should be normal and that the resulting solution should be clear and bright; this latter point is of special importance in connection with pharmaceutical practice. A saturated solution diluted with an equal volume of water should not yield any residue on filtration.


Fig. 5.—Solubility Apparatus.

For the accurate determination of solubilities the substance is placed in a suitable vessel along with the solvent and the whole is clamped in a thermostat arranged at the requisite temperature. The solvent and solute are kept in a state of brisk motion by means of an efficient stirrer. The state of the solution in comparison with saturation may be tested by withdrawing some of the solution and determining the amount of dissolved substance after, say, three, and again after four hours stirring. When the concentration of the solution no longer increases, the stirrer is removed and the solubility vessel stoppered. The excess of solute is allowed to subside and a measured quantity of the solution transferred by means of a delicate pipette to a tared weighing bottle; a short piece of glass tubing lightly filled with cotton-wool may be attached to the lower end of the pipette to act as a filter. Solubilities in volatile

solvents are best determined in the apparatus illustrated in fig. 5, which is similar to a small wash-bottle, having a plug of cotton-wool in the bottom of the exit tube and another in the mouthpiece. Evaporation of the solvent during transference to the weighing bottle is thus avoided. The solution is then weighed (it has already been measured) and the amount of solid in solution determined in an appropriate manner. When allowable, the determination is carried out most simply by evaporation to dryness in a tared dish and drying in the steam or air oven.

For the rough determination of solubilities in practice it is usually sufficient to weigh out one or more grams of the finely powdered substance and x gm. of water, the quantities depending on the known solubilities of the pure substance, and to see whether complete solution takes place. Warming may be necessary to effect solution within a reasonable time, in which case no crystallisation takes place when the solution is kept at room temperature. The possibility of supersaturation may be guarded against by adding a crystal of the substance to the solution. Some supersaturated solutions such as sugar syrups may take a considerable time to crystallise even if "seeded" with a crystal.

THE REFRACTOMETER.

There are several forms of refractometer on the market, *e.g.* the Pulfrich and Abbé refractometers, the butyro-refractometer, and the immersion refractometer. For the purpose of drug analysis, taking all things into consideration, the refractometer with water-jacketed prisms designed by Abbé is probably the most convenient; it also has the advantage of being the cheapest of those having a wide range.

The latest form of the **Abbé Refractometer** is shown in fig. 6. Full instructions for use are given with the instrument—the following abstract of these gives the necessary details:—



Fig. 6.—Abbé Refractometer.

A few drops of the liquid of which the refractive index is required are placed upon the lower of the two prisms, which has been released by opening the bayonet catch and opened by pulling downwards. The prisms are again closed, causing the liquid to be distributed over the entire space between them. The border line is brought within the field of the telescope by rotating the double prism by means of the arm on the left of the instrument, the mirror being moved until the brightest illumination is obtained. The border line is adjusted upon the point of

intersection of the cross wires in the telescope, when the index of refraction may be read off directly from the scale by means of the magnifier.

Under various circumstances the border line may not be sharp, owing to the presence of coloured bands; this is remedied by means of the compensator. The dispersion of the border line can be counteracted by rotating the screw head of the compensator until the line is colourless and sharp.

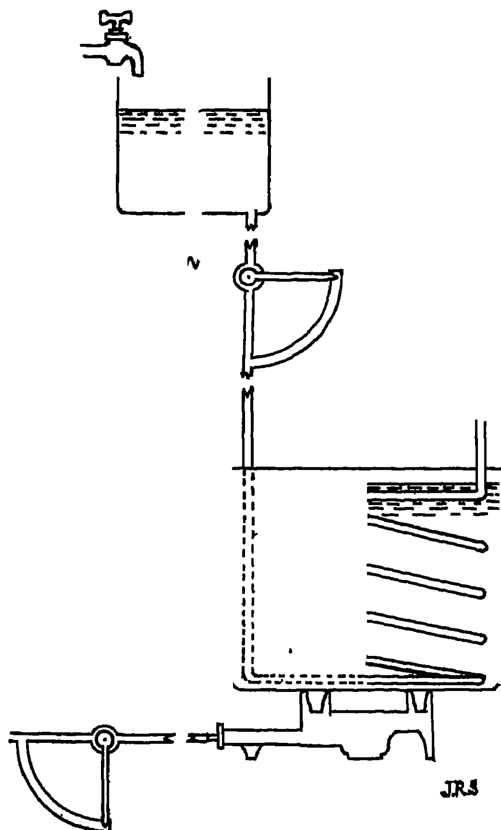


FIG. 7.—Heater for Refractometer.

As a rise or fall in temperature of 1° C. makes a difference of about 0·0004 in the index of refraction, the temperature of the liquid being tested must be known accurately. It is usual to determine refractive indices at certain fixed temperatures, as this is more satisfactory than employing haphazard temperatures and using corrections. Hence it may be necessary to keep the temperature of the refractometer constant for a considerable period. This is brought about by passing a current of water heated to the desired temperature through the prisms, the temperature being read off on the thermometer screwed thereinto. The current of water is kept at the desired temperature by means of a spiral heater and water-pressure regulators, which can be obtained from the makers of the refractometer. A much cheaper form, answering the same purpose, can, however, be easily made in the laboratory for a few shillings. An enamelled camp kettle of about four litres capacity, fitted with a lid, and about 15 feet of ¼-in. drawn brass tubing are required. The tubing is rolled up into a spiral of sufficient size to fit into the kettle, and two small holes are bored in the lid through which the ends of the spiral are passed, one end being connected with the refractometer and the other to a constant head of water. The connections and general arrangement are shown diagrammatically in fig. 7. It will be noticed that the water, after it enters the heater, has an entirely upward course, this being so arranged to prevent the accumulation of air bubbles.

The Working Temperature.—Unfortunately no temperature has been uniformly adopted as the one at which indices of refraction should be

taken. The majority of workers, however, seem to have adopted 25° C. for liquids and liquid oils, and 40° C. for those fats, etc., which are solid at 25° C. but liquid at this temperature, and figures for these temperatures are used in this book. A temperature of 20° C. is, however, more general for essential oils. These temperatures have also been adopted by the International Conference on Food Analysis.[1] In certain cases, however, *e.g.* hard paraffin and waxes, considerably higher temperatures have to be employed.

There is some uncertainty as to the actual correction which should be applied to convert indices of refraction from one temperature to another. For fixed oils it is about 0·00038 for each degree Centigrade, but it is better to take the readings at the exact temperature required and so avoid calculation.

Testing the Abbé Refractometer.—The makers recommend that the instrument be tested by using the testing plate which is supplied therewith, full details of which are given in the booklet accompanying it. As, however, the method is slightly involved, it is usually simpler to test the adjustment of the instrument by finding the index of refraction of distilled water and comparing it with the true value as set forth in the following table:—

TABLE IV.

INDEX OF REFRACTION OF DISTILLED WATER. (WAGNER.)

Temperature ° C.	Index of Refraction.	Temperature ° C.	Index of Refraction.
30	1·3320	22	1·3328
29	1·3321	21	1·3329
28	1·3322	20	1·3330
27	1·3323	19	1·3331
26	1·3324	18	1·3332
25	1·3325	17	1·3332
24	1·3326	16	1·3333
23	1·3327	15	1·3334

The instrument may also be tested by using one of the standard fluids which may now be obtained commercially. These have the advantage that the border line is usually much clearer than with water. The liquid usually employed is monobromonaphthalene, with a refractive index of 1·658 at 15° C.

In the event of repeated measurements of the refractive index of water or of a standard fluid showing a uniform departure of several units in the fourth decimal place, the refractometer should be adjusted in the following manner. The index of the instrument is set accurately to the value of the refractive index of the standard corresponding to the temperature of the prisms. The black milled ring should be turned until the border line coincides with the point of intersection of the cross lines. The adjustment should be verified by setting the border-line in the usual way, and taking repeated readings from the graduated scale.

[1] *Analyst*, 1911, 36, 536.

As a large number of the figures in literature are given as degrees on the butyro-refractometer scale, a table showing the relationship between these degrees and indices of refraction is given in the Appendix. This will also be found useful by those workers who already have a butyro-refractometer, for comparing their own readings with the standards given in this book.

The **Immersion Refractometer** of Zeiss (fig. 8) is now frequently used in analysis. It has the advantage of simpler manipulation and greater accuracy than the Abbé type, but, of course, it requires a much larger quantity of the liquid than the latter[1] Further, it has only a range from $n_D=1{\cdot}325$ to $n_D=1{\cdot}366$, so that its use is restricted to aqueous or alcoholic solutions of sugars, salts, etc., but by changing the prisms the range is considerably extended. Prisms are now made which give a range of 1·3254 to 1·4918. In order to take a reading, the refractometer is suspended with its lower end immersed in the liquid to be tested, which is contained in a beaker; the temperature is kept constant by a bath of water in which the beaker stands. The bottom of the trough is of glass, and light is reflected from the sky or other source of light by a mirror upwards through the bottom of the beaker. The position of the edge of the dark band on the scale is read off after adjusting the compensator as in the Abbé instrument. The scale is graduated in scale divisions from —5 to 105, which may be converted into refractive indices by means of the table supplied with the instrument, and which is reprinted in the Appendix of this book.

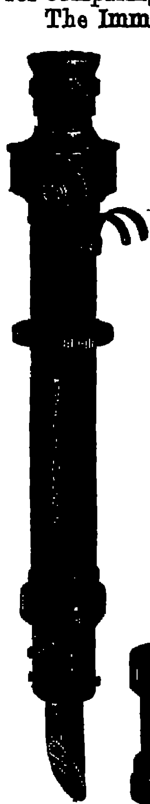


FIG. 8.—Immersion Refractometer.

THE POLARIMETER.

For the most accurate work a polarimeter reading to a hundredth of a degree is desirable, but such an instrument is somewhat expensive. A more simple form, however, reading to about a twentieth of a degree, will be sufficient for most purposes connected with drug analysis, and an instrument of this type will be described here.

It consists essentially of two Nicol's prisms, called respectively the polariser and the analyser, a scale graduated in degrees on which the rotation is read, and an arrangement for holding a tube containing the substance to be tested between the polariser and the analyser. An instrument of this type is shown in fig. 9. The readings are usually taken by the light of a sodium flame obtained by means of a sodium chloride pencil.[2] An ordinary 100-volt lamp may be used with a light filter of glass or a cell containing 15 mm. of a 6 per cent. potassium bichromate solution. For accurate work a mercury vapour lamp may be used, but the readings differ appreciably from those obtained with the sodium flame.

[1] With the use, however, of a special metal beaker which is attached to the instrument, refractions can be obtained on one or two drops.

[2] *See* McLachlan and Middleton, *Analyst*, 1927, 52, 639.

The instrument is used as follows: The sodium flame is lighted and placed about 3 or 4 in. from the end of the polarimeter opposite to that which bears the scale, and in such a position that the light shines into the end of the tube. The observer then looks into the telescope, which he pulls in or out until a clear and bright field is obtained, the analyser being moved round until the two halves of the field are of even brightness. If this point is not quite sharp the reading is being taken in the wrong quadrant, and the analyser should be moved through 90°. The scale reading should be taken for several settings of the instrument, approaching the point from both sides, and these should not differ by much more than 0·1°. The mean of these readings is the "zero" of the instrument which, if it is not exactly 0·0, must be subtracted from, or added to, as

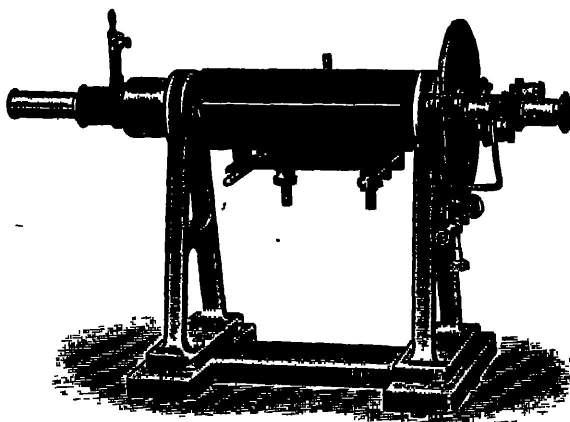


Fig. 9.—Polarimeter.

the case may be, the reading obtained with the substance that is being tested.

Having thus obtained the "zero" of the instrument, the 200 mm. tube is filled with the liquid to be tested and placed in the trough provided for its reception. On again looking into the telescope it will be found, if the liquid be optically active, that the two halves of the field are no longer of even brightness, and that the analyser has to be moved round in order to bring them once more into this condition.

Readings of this equi-bright point are taken until several concordant ones are obtained in succession, the mean of these, corrected for the "zero" of the instrument, giving the angle of rotation caused by the liquid in the tube. This observed rotation is usually denoted by α.

For successful reading the solution must be absolutely bright and transparent; colour is not so important, but even colour will make reading more difficult if it be at all deep. Solutions may often be clarified by careful filtration, but in the case of persistent haze it may be necessary to add 5 to 10 cc. of alumina cream (for preparation see Appendix) to a known volume of the liquid before filtration, the observed reading being corrected for the dilution. Troublesome colour may be removed by boiling with animal charcoal, but this method needs using with discretion. In

the case of many solutions the extra trouble of filtration may be avoided by using a 100 mm. or even a 50 mm. tube.

In the case of essential oils a 100 mm. tube is always used, as great accuracy is not essential, and the colour is very likely to interfere if a 200 mm. tube is used. Moreover, the reading gives what is called the optical rotation (not being quite the same as the $[\alpha]_D$) directly, without any calculation. In some cases of excessive colour, *e.g.* bergamot oil, a reading may be obtained by diluting with alcohol.

Specific Rotatory Power.—Although polarimetric results obtained in drug analysis are usually expressed in degrees of rotation for a 100 mm. tube, the method of calculation of the specific rotatory power is given here for the sake of completeness.

The Specific Rotatory Power is defined as *the angle of rotation produced by a liquid, which in the volume of 1 cc. contains* 1 *gm. of active substance, when the length of the column through which the light passes is* 100 *mm.* This is denoted by $\left[\alpha\right]_D^t$, where t is the temperature and D the light (sodium flame) which have been used.

For a homogeneous liquid,

$$\left[\alpha\right]_D^t = \frac{\alpha}{ld}$$

where l is the length of tube used, in decimetres, d is the density of the liquid, and α the observed rotation.

When the active substance is examined in solution the concentration must be taken into account, and if w is the number of gms. of active substance in 100 gm. of the solution, or c is the number of gms. in 100 cc. of solution—

$$\left[\alpha\right]_D^t = \frac{100}{lc} \quad \text{or} \quad \frac{100}{lwd}$$

In many cases the $[\alpha]_D$ of a substance in solution varies widely with the solvent and the concentration used. The subject is too wide for discussion here, save to remind the worker that where polarimetric figures are obtained on solutions both the solvent and the concentration should be stated.

The Effect of Temperature.—The specific rotatory power depends to a certain extent on the temperature. For all ordinary substances, however, with the notable exception of lævulose (and therefore of invert sugar), this does not introduce any great error, and observations are usually taken at room temperature. Figures in literature are usually given at 20° C.

THE DETERMINATION OF HYDROGEN-ION CONCENTRATION.

The determination of this factor is now a necessary part of the work of the majority of analytical laboratories. Hydrogen-ion concentration may be expressed in terms of a normal solution of hydrogen ions, but for convenience the expression pH is used. *p*H *is the Logarithm of the Reciprocal of the Concentration of Hydrogen Ions expressed in terms of a normal solution,* e.g. when $p\text{H}=2$, the hydrogen-ion concentration, or C_H, is 1×10^{-2}. *When* $p\text{H}=7{\cdot}12$ *at* 18° *C. the solution is neutral,* i.e. it contains equal numbers of hydrogen and hydroxyl ions. When the value of pH

is greater than this the solution is alkaline, but since the product of the concentration of hydrogen and hydroxyl ions must be constant, even strongly alkaline solutions show a definite though small concentration of hydrogen ions.

1. **THE ELECTROMETRIC METHOD.**—This is the most accurate method of determining *p*H. It gives excellent results, except in some cases where the presence of hydrogen causes changes in the solution.

(*a*) **The Hydrogen Electrode Method.**—This method of determination depends on the measurement of the potential of a platinum electrode coated with platinum black and saturated with hydrogen, in contact with the solution to be tested.

It is a difficult matter to measure the absolute difference of potential between a solid electrode and a liquid. The method used is to combine the electrode with a standard electrode of known potential, usually the saturated calomel electrode, which consists of mercury in contact with saturated potassium chloride solution saturated with calomel. The E.M.F. set up between this cell and a hydrogen electrode, under one atmosphere pressure of hydrogen gas, immersed in a normal solution of hydrogen ions is 0·250 volt at 18° C. The calomel cell is usually connected to the hydrogen electrode by a bridge of saturated potassium chloride solution. Simple forms of hydrogen and calomel electrodes are illustrated in fig. 10.

A simple arrangement for the purpose of measuring E.M.F. is illustrated in fig. 11. The circuit is illustrated diagrammatically in fig. 12. A dry cell, B, is connected to the circuit containing the potentiometer, P, and the galvanometer, MV, and the resistance, R. A second circuit containing the hydrogen electrode, H, and the calomel electrode, C, is also joined to the potentiometer. By depressing the standardising key, K, a current of definite potential is passed through the galvanometer by altering the resistance, R, until the galvanometer needle is at a definite point (100 on the scale). If the key, T, be now depressed, so as to bring the second circuit into action, the galvanometer needle moves backwards towards the zero mark. The potentiometer is now adjusted by means of the knob, S, until the galvanometer needle is at zero. The E.M.F. is then read off on the potentiometer scale in millivolts. From this reading by means of a scale the *p*H is found. In the instrument described, the Weston cell, W, is not included. When, however, a straight wire with sliding contact is used instead of a potentiometer the Weston cell is inserted at W, so that it can be switched into the circuit in place of the unknown, HJC. By balancing the current from the Weston cell against that of B, the potential fall per unit length of the wire P can be calculated, since the E.M.F. of the Weston cell is known, and in this way the instrument can be calibrated. The liquid to be tested is filled into the hydrogen electrode, and pure hydrogen gas (purified by passing through alkaline pyrogallol and alkaline permanganate) is bubbled through the tube for about ten minutes. The level of the electrode is then adjusted so that the platinum just touches the surface of the liquid. The reading is taken after making the necessary connections. The *p*H is calculated from the following formula :—

$$pH = \frac{E - 0{\cdot}250}{0{\cdot}0577},$$

where E is the measured potential in volts at 18° C.

2

The Preparation of the Hydrogen Electrode.—The hydrogen electrode (see fig. 10) consists of a small piece of platinum foil or wire thinly coated with platinum black. The electrode is first cleaned by dipping into a

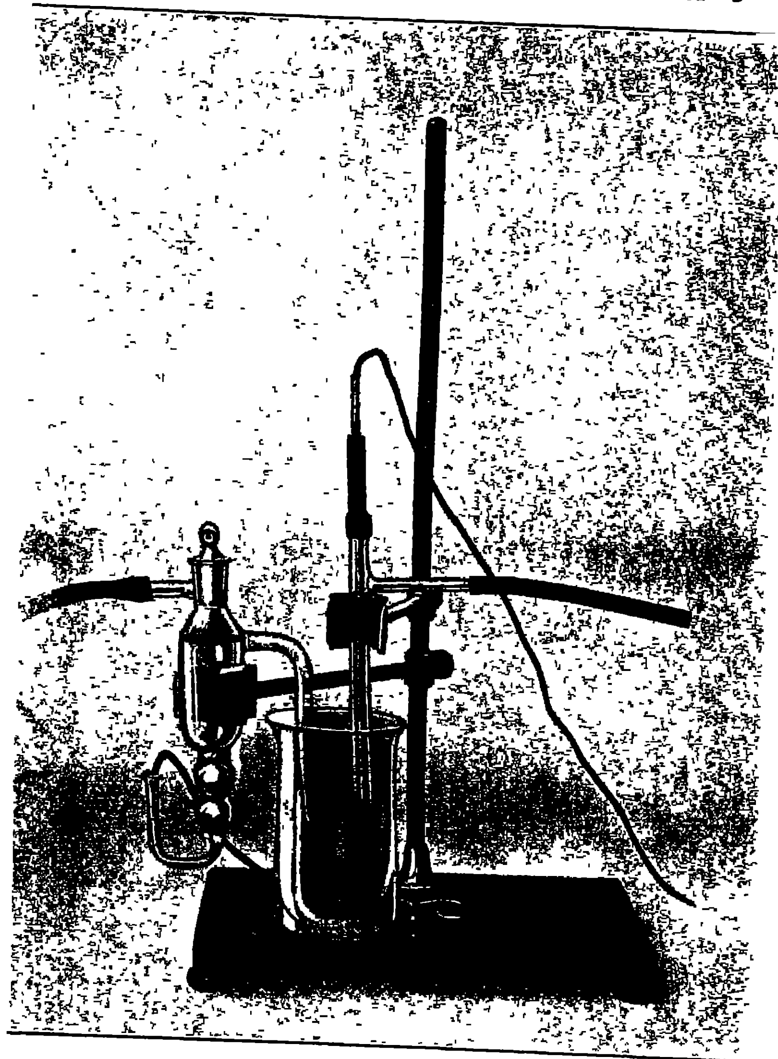


FIG. 10.—Hydrogen and Calomel Electrodes.

vessel containing a one-to-one dilution of hydrochloric acid into which dips an electrode. The treated electrode is made the positive pole and a current is passed from a 4-volt accumulator. The electrode is then dipped into a second cell containing platinum chloride solution, and a current is passed in the reverse direction until a thin uniform coating of platinum black is

obtained. The electrode is washed immediately with water and electrolysed in a vessel containing 10 per cent. sulphuric acid, so that it becomes saturated with hydrogen. Electrodes may be used repeatedly if kept clean and not allowed to dry. When used with organic liquids, however, they are liable to lose their sensitiveness after a short time.

The Preparation of the Saturated Calomel Electrode.—In the saturated calomel electrode (see fig. 10) a layer of mercury supports a layer of calomel in a saturated solution of potassium chloride, which is also saturated with the calomel. The calomel is carefully prepared in a pure condition by the following method: Pure mercury is dissolved in pure redistilled nitric acid, maintaining an excess of mercury. The solution is poured into a large excess of distilled water. Pure redistilled hydrochloric acid is then added

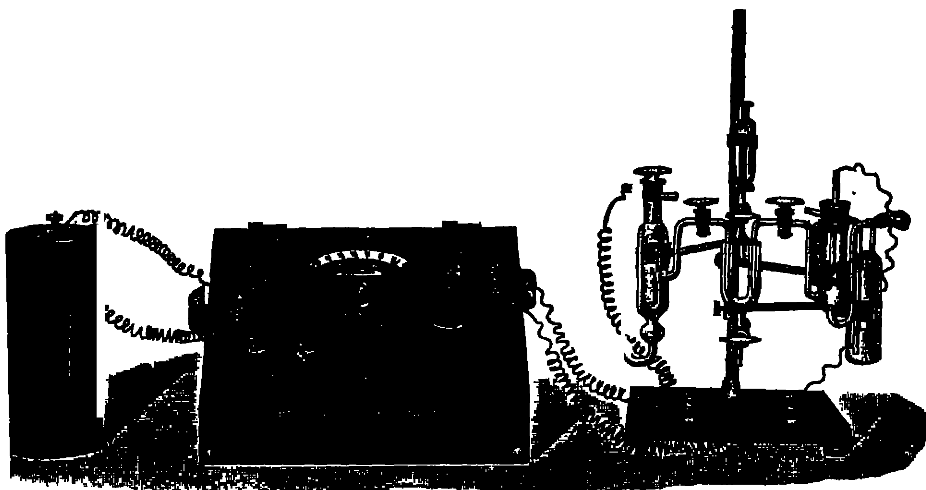


FIG. 11.—Apparatus for *p*H Determinations.

to the solution with constant stirring until all the mercury is precipitated. The precipitate is allowed to settle, washed thoroughly by decantation with distilled water, and finally filtered. A little free mercury should be present throughout the process. The calomel thus obtained is shaken several times with a saturated solution of potassium chloride and finally poured on to the top of the mercury in the electrode vessel so as to form a layer about 0·5 cm. thick. The vessel is then filled with a saturated solution of pure potassium chloride saturated with calomel.

(*b*) **The Quinhydrone Electrode Method.**—This method has proved a most convenient means of determining hydrogen-ion concentration. The use of hydrogen is eliminated. A platinum or gold electrode in contact with a mixture of hydroquinone and quinone shows a potential difference which varies according to the *p*H of the solution. Now quinone and hydroquinone combine in equimolecular proportions to form quinhydrone. In aqueous solutions this reaction is reversible, and since the solubilities are low the addition of solid quinhydrone is a convenient way of providing a solution with a mixture of quinone and hydroquinone. In order to determine the *p*H, therefore, all that is necessary is to add solid quinhydrone to

the solution to be tested and to measure the potential difference when connected with a calomel electrode exactly as in the case of the hydrogen electrode, except that the calomel electrode is connected to the positive side of the circuit instead of to the negative. Quinhydrone may be prepared by dissolving 25 gm. of hydroquinone in 100 cc. of hot water and adding 100 gm. of ferric ammonium sulphate dissolved in 300 cc. of warm water.

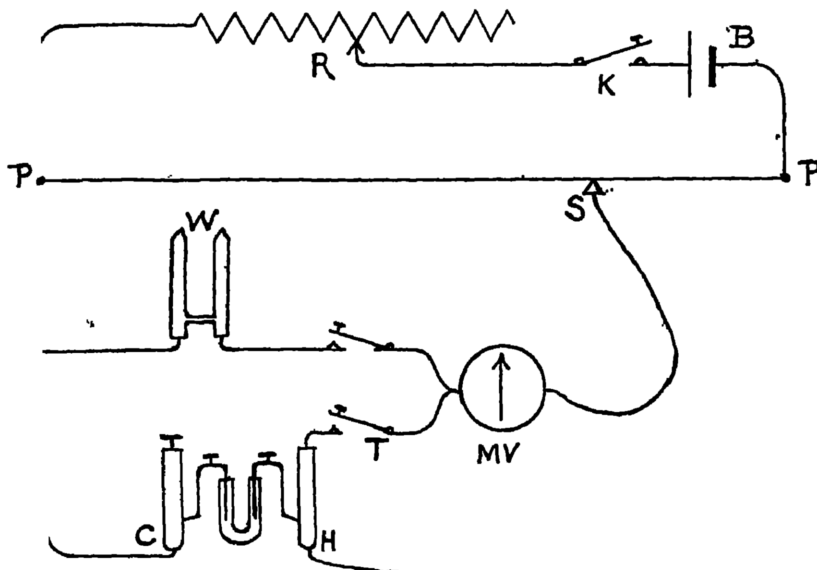


FIG. 12.—Circuit for *p*H Determinations.

After cooling on ice the deposited quinhydrone is filtered at the pump and washed with cold water.

The expression connecting *p*H and the E.M.F. of the system is :—

$$pH = \frac{0{\cdot}7175 - 0{\cdot}00084t - \pi - E_h}{0{\cdot}000198T}$$

where

t = temperature in degrees C.
T = absolute temperature,
π = E.M.F. in volts of the calomel electrode,
E_h = observed potential difference.

At 18° C., using a saturated calomel electrode—

$$pH = \frac{0{\cdot}4539 - E_h}{0{\cdot}0577}.$$

The electrodes used are of platinum or gold foil or wire. In order to make a determination, a pinch of quinhydrone is added to the liquid to be tested, so as to form a saturated solution. The potential difference is then measured in the ordinary way. The quinhydrone electrode can only be used in acid or neutral solutions (*p*H not greater than 8), and the results

TABLE V.

INDICATORS. *p*H VALUES.

	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0	10·0	11·0
Thymol blue .	Pink	Orange	Yellow	—	—	—	—	Yellow	Greenish	Blue	—
Bromophenol blue	—	—	Yellow	Green-ish	Blue Violet	—	—	—	—	—	—
Methyl red . .	—	—	—	Pink	Orange	Yellow	—	—	—	—	—
Bromocresol purple	—	—	—	—	Yellow	Greenish	Purple	—	—	—	—
Bromothymol blue	—	—	—	—	—	Yellow	Green	Blue	—	—	—
Phenol red . .	—	—	—	—	—	—	Yellow	Orange	Red	—	—
Phenolphthalein .	—	—	—	—	—	—	—	—	Colour-less	Pink	—
Thymolphthalein .	—	—	—	—	—	—	—	—	—	Colour-less	Blue
	$\frac{N}{10}$	$\frac{N}{10^2}$	$\frac{N}{10^3}$	$\frac{N}{10^4}$	$\frac{N}{10^5}$	$\frac{N}{10^6}$	$\frac{N}{10^7}$	$\frac{N}{10^8}$	$\frac{N}{10^9}$	$\frac{N}{10^{10}}$	$\frac{N}{10^{11}}$

Hydrogen Ion Concentration.

Acid — Neutral — Alkaline

are valueless if any chemical reactions occur between the quinhydrone and any constituent of the solution. Satisfactory results may be obtained with liquids such as solutions of alkaloids, blood serum, pituitary extracts, insulin, etc.

2. **THE COLORIMETRIC OR INDICATOR METHOD.**—This method, though sufficiently accurate for ordinary purposes, is not capable of as great accuracy as the electrometric method. It requires, however, no special apparatus, and a large number of determinations can be carried out at the same time. It is inapplicable to very dark solutions, though it may be used for coloured solutions if the colour is not too deep. The colorimetric method depends on the fact that the colour change of every indicator extends over a characteristic zone of hydrogen-ion concentration; if, therefore, the hydrogen-ion concentration of an unknown liquid lies within the range of a certain indicator we can determine the factor with accuracy if we can find a solution of known hydrogen-ion concentration which gives the same shade of colour when the indicator is added to it as the solution to be tested. The two essentials for this method are, therefore: (*a*) a complete series of indicators with well-marked colour changes covering a wide range of hydrogen-ion concentrations; (*b*) solutions of known hydrogen-ion concentration which are easily prepared and stable. In Table V. (p. 21) a series of indicators is given which show brilliant colour changes over a range of *p*H 1·0 to *p*H 11·0. Solutions of standard hydrogen-ion concentration may be prepared from the following four solutions together with *N*/10 hydrochloric acid and *N*/10 sodium hydroxide. By taking definite volumes of these solutions with varying volumes of *N*/10 hydrochloric acid and *N*/10 sodium hydroxide, solutions of any *p*H required may be obtained.

1. *Standard N/10 Sodium Citrate Solution.*—This is prepared by dissolving 21·008 gm. of pure citric acid in 200 cc. of *N*-sodium hydroxide solution and diluting to 1000 cc. with water.

0·1 *N*-Citrate Solution.	0·1 *N*-HCl.	*p*H.	0·1 *N*-Citrate Solution.	0·1 *N*-NaOH.	*p*H.
cc.	cc.		cc.	cc.	
1·0	9 0	1·17	9·5	0·5	5·02
2·0	8·0	1·42	9·0	1·0	5·11
3·0	7·0	1·93	8·0	2·0	5·31
3·33	6·66	2·27	7·0	3·0	5·57
4·0	6·0	2·97	6·0	4·0	5·97
4·5	5 5	3·36			
4·75	5·25	3·53			
5 0	5·0	3·69			
5·5	4·5	3·95			
6 0	4·0	4·16			
7·0	3·0	4·45			
8 0	2·0	4·65			
9 0	1·0	4·83			
9·5	0·5	4·89			
10·0	0·0	4·96			

2. *Standard N/5 Sodium Borate Solution.*—This is prepared by dissolving 12·404 gm. of pure boric acid in 100 cc. *N*-sodium hydroxide solution and diluting to 1000 cc. with water.

0·2 *N*-Borate Solution.	0·1 *N*-HCl.	*p*H.	0·2 *N*-Borate Solution.	0·1 *N*-NaOH.	*p*H.
cc.	cc.		cc.	cc.	
5·5	4·5	7·94	9·0	1·0	9·36
5·75	4·25	8·14	8·0	2·0	9·50
6·0	4·0	8·29	7·0	3·0	9·68
6·5	3·5	8·51	6·0	4·0	9·97
7·0	3·0	8·68	5·0	5·0	11·08
7·5	2·5	8·80			
8·0	2·0	8·91			
8·5	1·5	9·01			
9·0	1·0	9·09			
9·5	0·5	9·17			
10·0	0·0	9·24			

3. *Standard (M/15) Potassium Dihydrogen Phosphate Solution* is prepared by dissolving 9·078 gm. pure potassium dihydrogen phosphate (KH_2PO_4) in 1000 cc. water.

4. *Standard (M/15) Sodium Phosphate Solution* is prepared by dissolving 23·87 gm. pure sodium phosphate ($Na_2HPO_4.12H_2O$) in 1000 cc. water.

The two last solutions are used in combination.

PHOSPHATE STANDARDS.

M/15 Na_2HPO_4 Solution.	M/15 KH_2PO_4 Solution.	*p*H.	M/15 Na_2HPO_4 Solution.	M/15 KH_2PO_4 Solution.	*p*H.
cc.	cc.		cc.	cc.	
0·0	10·0	4·49	6·0	4·0	6·98
0·1	9·9	4·94	7·0	3·0	7·17
0·25	9·75	5·29	8·0	2·0	7·38
0·5	9·5	5·59	9·0	1·0	7·73
1·0	9·0	5·91	9·5	0·5	8·04
2·0	8·0	6·24	9·75	0·25	8·34
3·0	7·0	6·47	9·9	0·1	8·68
4·0	6·0	6·64	10·0	0·0	9·18
5·0	5·0	6·81			

The following solutions are also required :—

N/10 Sodium Hydroxide Solution (free from Carbonate).—One hundred grams of pure sodium hydroxide are dissolved in 100 cc. water in a flask covered with tin-foil, and allowed to stand overnight for the carbonate to

settle. The solution is then filtered quickly with the aid of the pump through a hardened filter. 10 cc. are diluted to about *N*/5 strength with distilled water free from carbon dioxide, standardised against potassium hydrogen phthalate to phenolphthalein, and diluted to *N*/10 strength. This solution is stored in a bottle coated with paraffin wax and connected by a glass tube with a burette. The bottle and the burette have side-tubes joined to soda-lime tubes to prevent the entrance of carbon dioxide.

N/10 *Hydrochloric Acid.*—The ordinary laboratory solution may be used.

The above solutions, with the exception of the *N*/10 sodium hydroxide, are kept in well-stoppered resistant glass reagent bottles. The only other apparatus required consists of burettes, graduated pipettes, suitable dropping bottles for the indicators, and racks for the test-tubes.

Indicator Solutions.—The following table shows a complete series of indicators which may be used for solutions from *p*H=1 to *p*H=11. These indicators are readily obtainable on the market.

TABLE VI.

	Strength of Solution.	Range of *p*H.
	Per Cent.	
Thymol blue . . .	0·04 in water . . .	{1·2 to 2·8
		{8·0 ,, 9·6
Bromophenol blue . .	0·04 ,, ...	2·8 ,, 4·66
Methyl red . . .	0·02 in 50 per cent. alcohol	4·4 ,, 6·0
Bromocresol purple .	0·04 in water . . .	5·2 ,, 6·8
Bromothymol blue .	0·04 ,, ...	6·0 ,, 7·6
Phenol red . . .	0 02 ,, ...	6·8 ,, 8·4
Thymolphthalein . .	0·04 in alcohol . . .	10·0 ,, 11·0

Method of Determination.

1. *For Clear or Turbid Liquids* (*free from Colour*).—The solution to be ested is tried with a compound indicator or with various indicators until me is found which gives a tint lying between its extremes of colour. 10 cc. f the solution are then run into a clean test-tube, washed with neutral listilled water, and 5 or more drops of the indicator solution are added. Vith a little practice it is easy to judge from the shade of colour roughly hat the *p*H value is. 10 cc. of a solution of this *p*H value are then preared in another test-tube from the standard solutions by consulting the ables, *e.g.* if the solution gives a neutral colour with bromophenol blue, he *p*H may be judged to be about 3·5. From the tables we see that a iixture of 4·75 cc. of *N*/10 citrate solution and 5·25 cc. of *N*/10 hydrohloric acid has a *p*H value of 3·53. This mixture is therefore prepared by inning in the solutions from burettes or graduated pipettes. Five drops the indicator are added and the colours compared. If the shades of lour do not match, another tube of a different *p*H value is prepared itil an exact match is obtained. Tubes of standard colour may be tained for the purpose of comparison and save the trouble of preparing

standard solutions. Colour charts may also be obtained for the same purpose.[1]

2. *For Coloured Liquids.*—For this purpose the piece of apparatus known as a comparator is used (see fig. 13). It consists of a cubical block of wood of 3½ inches side, with four holes bored vertically to hold four test-tubes. Two holes are also bored horizontally completely through the block, so that it is possible to look through two pairs of test-tubes simultaneously. In hole No. 1 is placed the tube containing 10 cc. of the solution to be tested and 5 drops of indicator. Hole No 2, behind this, holds a tube containing 10 cc. of distilled water. In No. 3 we have the tube containing 10 cc. of the standard solution with 5 drops of indicator, and, behind this, in No. 4, is a tube containing 10 cc. of the coloured solution. In this way the colour is compensated, and we can compare the shades of colour without interference from the colour of the solution. If the colour of the solution is very dark, it may not be possible to distinguish the colour of the indicator, and recourse must be had to the electrometric method. Where a large number of determinations has to be made it is convenient to have racks holding test-tubes containing a series of standard solutions with the indicator, so that the tubes can be easily picked out for comparison and replaced. In this way a large number of solutions can be dealt with in a very short time. With practice it is quite easy to get a rough idea of the pH value of a solution by merely adding the indicator without the use of standard solutions, and in many cases this may be all that is required.

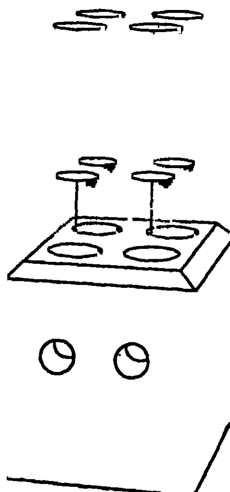


FIG. 13.—Comparator.

Mixed indicators are available which give a continuous change of colour from $pH=4$ to $pH=11$, passing through the colours of the spectrum from red to violet. These indicators are very useful for the approximate determination of pH, and largely replace the use of litmus paper for determining the reaction of a liquid.

Volumetric Analysis.[2]

1. **The Use of Indicators.**—The end product of the titration of an acid with a base has a definite hydrogen-ion concentration depending on the degree of hydrolysis of the salt formed, and on the concentration and temperature of the solution. For most practical purposes the last two factors may be neglected. The pH of the end product is therefore dependent on the nature of the salt formed, and our means of determining when the end point is reached depends on measuring this pH by the use of indicators which change colour at this pH. For example, when ammonia is titrated with hydrochloric acid the solution of ammonium chloride formed has $pH=5{\cdot}2$. Methyl red, which changes colour from pH 4·4 to 6 is therefore a suitable indicator for this titration.

[1] *Colour Chart of Indicators*, by W. M. Clark. Williams & Wilkins Co., Baltimore, U.S.A.

[2] For the standardisation of acid and alkali, see Appendix.

In a satisfactory titration, as carried out in the ordinary way, 1 drop of standard solution should bring about the colour change of the indicator. In many cases, however, the end point is not sharply defined. Such titrations may be made more accurate by titrating to a definite shade of colour corresponding to the pH of the end point of the titration, and comparing the colour either with a solution of standard pH or with a colour chart.

The following indicators will be found useful for analytical work and generally superior to the older indicators such as methyl orange. (For pH range and colour change, see Table V, p. 21).

Thymol Blue generally replaces phenolphthalein for the titration of weak acids with strong bases. The alkaline blue colour is more easily seen in coloured solutions.

Phenolphthalein gives accurate results, and is preferred by many for its one-colour change. The proportion of phenolphthalein used should always be the same, as the results obtained vary with different amounts of indicator.

Bromophenol Blue is of similar range to methyl orange, and generally replaces it for the titration of weak bases such as certain alkaloids with strong acids, and strong bases with strong acids, or *vice versa*. It is unaffected by carbon dioxide.

Methyl Red is the best indicator for moderately weak bases such as ammonia or certain alkaloids.

Phenol Red is of value for titrations of acids which are too strong to give accurate results with phenolphthalein or thymol blue, *e.g.* salicylic acid.

The following mixed indicators are of use in analysis :—

Methyl-Thymol Blue (Methyl red, 1 ; thymol blue, 3) is useful for the titration of strong acids and bases. The neutral colour of the indicator is from $p\mathrm{H}=6$ to 8. Excess of alkali gives a blue colour, excess of acid a red colour. As long as the colour at the end of the titration is yellow, therefore, the correct end point has been attained. The titration cannot be overshot by careless manipulation without its being apparent.

Phenol Violet (Phenolphthalein, 1 ; thymol blue, 6). The colour change is similar to thymol blue, except that the further addition of alkali causes the blue colour to change to violet. Overshooting is thus avoided. This indicator is especially valuable for saponification values.

A table of acids and bases with the correct indicators for use in each case [1] is given on pp. 27 and 28.

2. **Electrometric Titration.**[2]—Since the process of titration of acids or bases consists in bringing the solution to a definite hydrogen-ion concentration, it is clear that accurate results may be obtained without the use of indicators by continuing the addition of acid or alkali until the pH as determined electrometrically (see p. 17) reaches the point required. The solution is contained in a beaker provided with a stirring arrangement. A hydrogen electrode and a calomel electrode dip into the solution. The addition of acid or alkali from a burette is continued until the reading of the potentiometer corresponds with the pH of the end point.

[1] Lizius and Evers, *Analyst*, 1922, **47**, 337.
[2] See Callan and Horrobin, *J. Soc. Chem. Ind.*, 1928, **47**, 329T.

The advantage of the electrometric method is that it can be used in cases where indicators are useless, *e.g.* in the titration of dark coloured solutions or of solutions containing proteins, which interfere with the colour changes of indicators.

TABLE VII.

Acids.

Acid.	pT.	Indicators.	End Colour.	Remarks.
Hydrochloric, Hydrobromic, Hydriodic, Sulphuric	7·0	Methyl-thymol blue	Yellow	
		Methyl red	Orange	
		Bromophenol blue	Green	
Picric acid	7·0	Methyl red	Yellow	
Saccharin	7·1	Phenol red	Orange	
Salicylic acid	7·2	"	"	
Nitric acid	7·5	"	"	
Hippuric acid	7·5	"	"	
Fumaric acid	7·5	"	"	To neutral salt.
Benzoic acid	7·6	"	"	
Formic acid	7·8	"	"	
Lactic acid	7·8	"	"	
Cinnamic acid	8·0	"	Red	
Oxalic acid	8·0	"	"	
Acetylsalicylic acid	8·0	"	"	
Tartaric acid	8·1	"	"	
Valeric acid	8·3	Thymol blue or Phenol violet.	Green	
Carbonic acid	8·4	" "	"	To bicarbonate.
Maleic acid	8·5	" "	"	To neutral salt.
Malonic acid	8·5	" "	"	
Boric acid with glycerin	8·6	" "	"	
Acetic acid	8·8	Thymol blue or Phenol violet	Blue	
Phthalic acid	8·8			
Succinic acid	8·8	or Phenol-thymol-phthalein.	Pink	
Malic acid	8·8			
Citric acid	9·5	Phenol violet	Violet	
Oleic acid	9·5	or Phenol-thymol-phthalein.	"	
Diethylbarbituric acid	10·2	Thymol violet	Green	To standard colour.
Phosphoric acid or Glycerophosphoric acid	4·5	Bromophenol blue	Blue (max.)	To acid salt.
	9·1	Thymol blue or Phenol blue.	Blue	To normal salt.
Hypophosphorous acid	5·5	Methyl red	Orange	
Boric acid without glycerin.	11·1	Too weak for titration.		
Phenol	12·0			

[Table VII.—*Continued.*

TABLE VII.—*Continued.*

BASES.

Base.	pT.	Indicator.	End Colour.	Remarks.
Strong bases	7·0	Methyl-thymol blue	Yellow	
		Methyl red	Orange	
		Bromophenol blue	Green	
Nicotine	5·5	Methyl red	Orange	
Homatropine	5·5	,,	,,	
Ammonia, Morphine, Codeine	5·2	,,	,,	
Atropine, Strychnine, Brucine, Ethylmorphine	5·0	,,	,,	
Diacetylmorphine, Emetine	4·9	,,	Orange-red	
Cocaine, Pilocarpine	4·7	,,	Red	Direct titration.
		Bromophenol blue	Blue (max.)	Back ,,
Piperazine	3·7	,,	Green	
Pyridine	3·6	,,	,,	
Aniline	2·8			Not sharp.
Quinine, Cinchonine (to acid salt).	3·5	,,	Standard colour.	,,
Cinchonidine, Quinidine (to neutral salt)	5·6	Methyl red	,,	,,

SALTS.

Salt.	pT.	Indicator.	End Colour.	Remarks.
Borax	5·2	Methyl red	Orange	
Sodium carbonate to bicarbonate.	8·4	Phenol violet or Thymol blue.	Yellow	
Sodium phenate	6·5	Phenol red	,,	
Sodium dihydrogen phosphate (to acid salt).	4·5	Methyl red	Red	To maximum colour.
Sodium acid phosphate (to normal salt).	9·1	Thymol blue or Phenol violet.	Blue	To standard colour.
Sodium arsenate	5·5	Methyl red	Orange	,, ,,
Caffeine citrate	9·5	Phenol violet	Violet	
Caffeine hydrobromide	7·2	Phenol red	Orange	
Quinine acid salts (to neutral salt).	5·6	Methyl red	,,	,, ,,

All the above results were obtained with decinormal solutions. Titrations with seminormal or normal solutions are naturally sharper and more accurate.



PART II.

INORGANIC DRUGS AND CHEMICALS.[1]

SECTION I.

INTRODUCTION.

UNDER this heading will be included individual tests and standards for all those chemicals and reagents which are likely to be met with in ordinary work. Before proceeding to this detailed description it has, however, been thought better, in order to save needless repetition, to group certain widely used tests together. In the body of the section the various impurities most likely to be present are mentioned, and directions are given for any tests that are likely to cause trouble. Limits of impurities have been given generally for substances of pharmaceutical quality. It should be understood that these limits may not necessarily be sufficiently stringent where the chemical is to be used as a reagent, and may be too stringent for ordinary commercial purposes.

DETERMINATION OF ARSENIC.

The method now official is a modification of the Gutzeit method,[2] which depends on the production of a yellow stain on paper saturated with mercuric chloride by the arsenic liberated as hydrogen arsenide, and the comparison of the stain so produced with that given by a known amount of arsenic.

Arsenic in chemicals is expressed as parts of arsenic per million, the term "arsenic" here being used to indicate arsenious oxide, As_2O_3.

THE ZINC AND ACID METHOD.

Apparatus.—An ordinary 4-oz. wide-mouthed bottle is closed with a rubber bung through which passes a glass tube about 300 mm. long and 5 mm. in diameter, slightly drawn out at the lower end and having a small hole blown in its side near this end, to prevent water from bubbling up the tube. A small plug of non-absorbent cotton-wool is pushed down to near the lower end of the tube which is then filled to within 2 cm. of the top with plumbised wool, prepared by soaking cotton-wool in 10 per cent. lead acetate solution and drying in the oven. This absorbs any hydrogen

[1] Salts of Inorganic Bases with Organic Acids are included in this section.

[2] Hill and Collins, *C. & D.*, 1905, 67, 548.

sulphide which may be evolved. A small plug of absorbent wool is inserted above this.

Mercuric Chloride Papers.—These are circles or squares of plain white filter paper 1½ to 2 in. across, which have been soaked in a saturated solution of mercuric chloride in alcohol and dried without heat in the dark. (The presence of small crystals of mercuric chloride on the paper is to be avoided, as they may drop down the tube on to the wool and absorb the arsenic before it reaches the paper.) Strong sunlight affects the mercuric chloride papers and also the arsenic stain, and tests should be carried out in diffused light. The mercuric chloride papers should be stored in the dark.

Hydrogen sulphide and hydrogen phosphide both give yellow stains with mercuric chloride paper. These are distinguishable from arsenic stains with a little experience, but care should be taken to exclude the possibility of error.

Reagents.—*Hydrochloric Acid* should not contain more than 0·1 part of arsenic per million and should be free from iron.

Stannous Chloride Solution, prepared from strong solution of stannous chloride by adding an equal volume of hydrochloric acid and boiling until the original bulk is reached. If 10 cc. of the solution are distilled with 10 cc. of hydrochloric acid and 6 cc. of water the first 18 cc. of the distillate should not give a stain deeper than the standard stain, showing that not more than 1 part per million of arsenic is present.

Bromine Solution.—Prepared by dissolving 30 gm. of bromine and 20 gm. of potassium bromide in water and diluting to 100 cc. It should not contain more than 1 part of arsenic per million.

Stannated Hydrochloric Acid contains 1 cc. of stannous chloride solution to 100 cc. of hydrochloric acid.

Brominated Hydrochloric Acid.—Prepared by adding 1 cc. of solution of bromine (*q.v.*) to hydrochloric acid and diluting to 100 cc.

Zinc.—The zinc should be granulated in lumps of suitable size, about the size of small peas. When 7 gm. are tested by the Gutzeit test with 20 cc. of stannated hydrochloric acid not more than the faintest stain should be obtained. Tests should also be carried out on the same amount with the addition of 0·5 and 1 cc. dilute arsenic solution. The stains should be well defined, and of proportionate intensity.

Arsenic Solution.—1 cc. of hydrochloric acid solution of arsenic (B.P.) diluted to 1000 cc. with water. 1 cc. contains 0·00001 gm. arsenic (As_2O_3).

Method.—A small inverted cork or bung is fitted over the open end of the tube so that the end of the tube is level with the surface of the cork. A circle of mercuric chloride paper is placed over the end of the tube and a larger glass tube about 1 in. long is fitted to the cork so that one half of it projects above the level of the cork. A second cork is then fitted into this end, so that the paper is pressed tightly against the first cork and the edge of the tube.[1] The solution to be tested is prepared in various ways according to the requirements of each individual case (which will be described under each substance where it differs from the following), but in the usual way the required quantity of the substance is dissolved in 50 cc. of warm water in the bottle, 10 cc. of stannated hydrochloric acid and 7 gm. of zinc are added and the bung and tube quickly placed in position. The action is allowed to continue for at least half an hour. It is hastened by

[1] Stubbs, *Analyst,* 1927, **52**, 700. (See fig. 14, p. 32.)

placing on the top of the water-oven. The stain, if any, is then compared with the standard stain prepared simultaneously as described below; stains fade on keeping and should be compared at once.

Preparation of the Standard Stain.—1 cc. of the dilute arsenic solution is treated by the above process. The standard stain is therefore produced by 0 00001 gm. of As_2O_3. A substance, 1 gm. of which produces a stain equal to the standard stain, contains 10 parts of arsenic per million. By dipping the stain into a solution of hydrobromic acid it is darkened in colour and comparisons may be more easily made, or the papers may be made directly from mercuric bromide solution. Treatment with potassium iodide blackens the stain and renders it permanent.

THE ELECTROLYTIC METHOD.—The method described is based on the papers of Monier Williams[1] and Callan,[2] with some modifications which have been found useful by the authors. The apparatus is illustrated in fig. 14. It consists of a lead beaker which functions as the anode, and is connected by a wire to the positive pole of the current source. In this beaker stands a thin porous pot. In the latter again stands a glass vessel which is open at the bottom and rests on the bottom of the porous pot. This vessel has two exit tubes, one of which is fitted with a rubber stopper through which passes a glass rod round which a strip of lead is wound and forms the cathode, being connected by a wire to the negative terminal of the current source. The cathode is best made by cutting a piece of lead-foil in the shape of fig. 15 and rolling it round a glass rod, beginning at A. It can then be slipped through the tube, unrolled, and connected up after stoppering at the top. The other exit tube is connected by a ground-in stopper with a tube filled with non-absorbent cotton-wool. This again is connected by a second ground-in stopper with a tube which is filled with plumbised cotton-wool to within 1½ in. of the top, a small plug of absorbent wool being inserted at the top. The mercuric chloride paper is fixed on as described in the ordinary Gutzeit test.

Sulphuric acid of 15–20 per cent., containing 0·025 per cent. of cadmium sulphate, is used as the conducting liquid.

The weight of the substance required is dissolved in or mixed with 35 cc. of the dilute sulphuric acid, and poured into the porous pot, which is placed in the lead beaker with sufficient dilute sulphuric acid to reach the same level as the liquid inside the porous pot. The glass apparatus is now placed inside the porous pot, and the mercuric chloride paper fixed in position.

A direct current of 3 to 6 ampères is passed, the potential difference between the electrodes being 7 to 9 volts. The evolution of arsenic is usually complete after half an hour, but in the case of a stain being obtained the current should be allowed to flow for a further half-hour with a fresh mercuric chloride paper, in order to make sure that all arsenic has been evolved. The same methods of obtaining standard stains are used as in the acid and zinc method described above. In order that the cathode may remain sensitive it must be kept clean; after using it several times the film of cadmium which forms should be scraped off. Reversing the current ruins the cathode. The cathode cannot always be relied on to be equally sensitive if a second test is put on immediately after the first,

[1] *Analyst*, 1923, **48**, 112.
[2] *J. Soc. Chem. Ind.*, 1924, **43**, 168T.

but it regains its activity after standing in water. The cathode can be re-sensitised, if for any reason it has become insensitive, by washing with water and standing in very dilute nitric acid ; any deposit is then removed

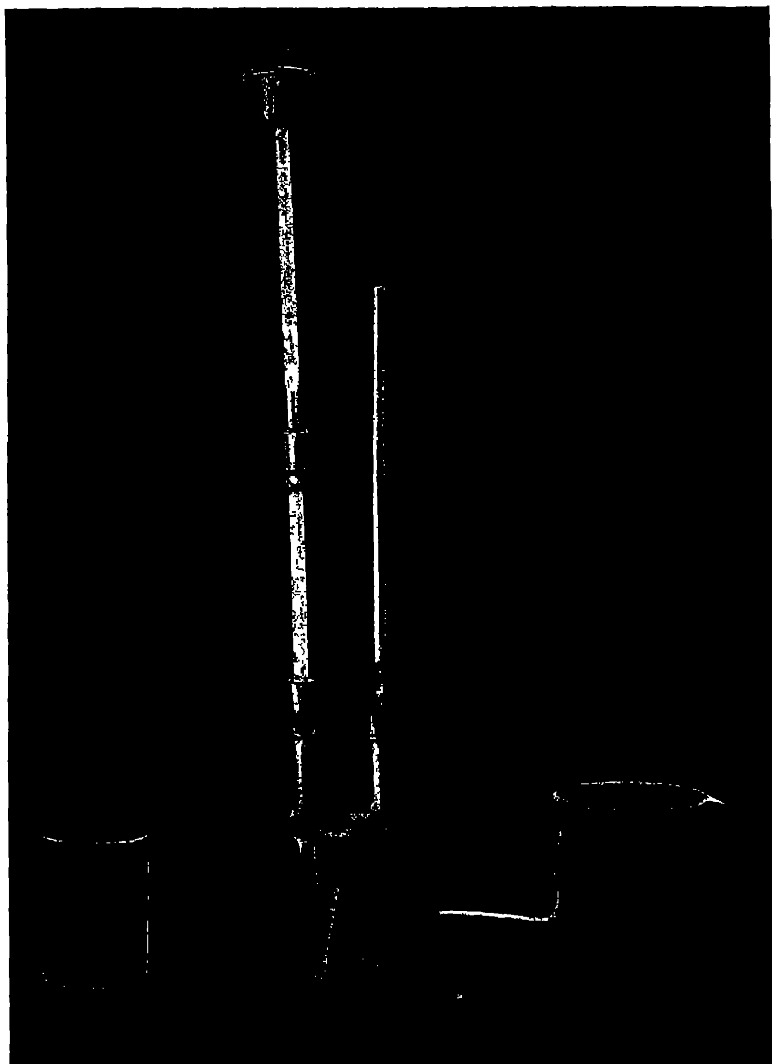


FIG. 14.—Arsenic Apparatus.

by rubbing with cotton-wool, and after thorough washing the cathode is allowed to stand in a dilute solution of cadmium sulphate for about an hour, finally being washed with distilled water. Most organic substances can be tested for arsenic by the electrolytic method without preliminary

treatment, but where it is desired to destroy the organic matter the substance may be treated with 25 cc. of a 20 per cent. solution of magnesium nitrate (arsenic free), evaporated down, and carefully ignited at a low temperature. Bromides or iodides are apt to contaminate the porous pot with bromine or iodine. This can be removed by soaking in a solution of sodium bisulphite, with subsequent washing. Special methods of preliminary treatment will be described under individual chemicals, but a few of the more generally applicable methods are given below.

Chlorides, Bromides, and Iodides.—On account of the evolution of chlorine, bromine, or iodine these salts cannot be directly electrolysed. Two gm. of the substance may be evaporated with 2 cc. of sulphuric acid until fumes of sulphur trioxide are evolved; the residue may then be treated in the ordinary way.

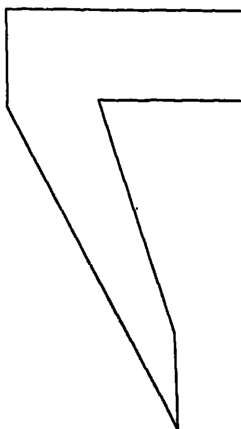


FIG. 15.—Lead Electrode.

Another method which has proved satisfactory is to fill up the outer chamber with 10 per cent. arsenic-free sodium thiosulphate solution instead of with sulphuric acid. Some sulphur is deposited, but this is easily washed off the porous pot, and the accuracy of the determination is unaffected.

Chlorates may be treated in the same way as hypophosphites without the addition of potassium chlorate.

Organic compounds may usually be treated directly without destruction of the organic matter, but it is better to warm with the sulphuric acid for about 15 minutes on the water bath before transferring to the porous pot. A few cc. of amyl alcohol (arsenic-free) should be added if frothing is likely to cause trouble.

Hypophosphites, Phosphites, and Sulphites.—The required amount is warmed on the top of the water bath with an equal weight of arsenic-free potassium chlorate and 35 cc. of cadmiumated sulphuric acid until no more chlorine is evolved. The solution is then transferred to the electrolytic apparatus, and the test completed as usual.

THE DETERMINATION OF LEAD.

The method now generally used for the determination of minute traces of lead in chemicals is colorimetric, and is based on the original work of Warington.[1] A large number of papers have appeared from time to time dealing with this matter, but the differences of opinion are largely in matters of detail. The following method, or slight modifications of it to suit the convenience of various workers, will be found both speedy and sufficiently accurate for ordinary routine work. It is based on the method adopted by the British Pharmacopœia with some modifications suggested by the authors.

It was first pointed out by C. A. Hill that in the colorimetric test of Warington the coloration produced by a given amount of lead is con-

[1] *J.C.S.*

siderably affected by the presence of metallic salts, and that different salts affect the darkening to varying extents. He found, however, that for any one salt the effect in the colour produced is independent of the concentration of the salt within wide limits; the method here given is based upon this fact. The standards are made with a solution containing a small amount (usually about one-third of that in the primary solution) of the salt which is being tested, called the control, instead of being made with distilled water, so that the actual amount of salt in which the lead is really determined is given by subtracting the weight taken in the control solution from that in the primary solution. The following solutions are required for the process:—

Strong Lead Solution.[1]—1·599 gm. of pure lead nitrate and 50 cc. of concentrated nitric acid are made up to 100 cc. with distilled water. One cc. of this solution contains 0·01 gm. Pb.

Dilute Lead Solution.—1 cc. of the above strong lead solution, measured by means of a carefully graduated slow-delivery pipette, is diluted to 100 cc. with water. 1 cc. of this solution contains 0·0001 gm. of Pb. It is much better freshly prepared, but frequently it will keep for several weeks without any appreciable diminution in strength.

Potassium Cyanide Solution.—10 gm. of potassium cyanide (98 per cent.) are dissolved in water, 2 cc. of hydrogen peroxide (10 vols.) added, and the whole diluted to 100 cc.

Sodium Sulphide Solution—A 10 per cent. solution of crystallised sodium sulphide in water.

Glacial acetic acid and ammonia solution are also required. All the reagents should be tested under the conditions of the experiment to make sure that they are free from lead. It is also advisable to see that the potassium cyanide solution has no effect on the coloration due to lead sulphide.

General Method of Working.—22·5 gm. (or any other convenient quantity, the quantities of the other reagents being changed in proportion) of the substance are added to water, 1 cc. of glacial acetic acid added,[2] and the whole diluted to 150 cc. The solution of the salt may be accelerated by warming, but the liquid must be again brought to laboratory temperature before proceeding with the test. If the solution is not perfectly clear and bright it should be filtered.

50 cc. of this solution (corresponding to 7·5 gm. of the substance) are placed in a 50 cc. Nessler cylinder, and 16·5 cc. of the solution (corresponding to 2·5 gm. of the substance) in each of three others. 3 cc. of the potassium cyanide solution are added to each, and the liquid made just alkaline with ammonia. Two drops of the sodium sulphide solution are then added to the first cylinder, and if no darkening occurs the substance may be considered to be free from lead. Should darkening occur the amount of lead present is determined by adding, say, 0·5 cc. of the diluted lead solu-

[1] When for any reason the lead is determined in acetic acid solution, the standard solution is better made from the acetate. For this purpose, 1·831 gm. of pure crystallised lead acetate are dissolved in water containing 5 cc. of glacial acetic acid and made up to 100 cc. Then 1 cc.≡0·01 gm. Pb. A dilution from this is made in the same manner as for the nitrate solution.

[2] To dissolve any minute particles of metallic lead and to prevent adsorption of dissolved lead by the filter paper (*Y.B.P.*, 1912, 501), should it be necessary to filter the liquid.

tion (1 cc. of which is equivalent, in the quantities used, to 20 parts of Pb per million in the substance) from a delicate burette to one of the other cylinders (the "control" solution), diluting to the mark with water, adding 2 drops of the sodium sulphide solution, and comparing the colour produced with that in the "primary" solution. Should the colour be of equal intensity in the two cylinders the substance contains 10 parts of Pb per million; if the two colours are different further standards are made in a similar manner, using more or less of the lead solution as may be required until a match has been obtained. The number of cc. of the lead solution used multiplied by 20 gives the parts of Pb per million in the substance used. The cylinders are matched by placing them on a white tile and viewing them from above—it is sometimes an advantage to raise the cylinders a few inches from the tile when viewing them. Both the bottom of the cylinder and the tile should be dry.

Where a number of samples of the same substance have to be examined at one time, a large amount of time and trouble are often saved by weighing out 5 gm. of each, dissolving in 50 cc. of water, and adding ammonia, cyanide, and sulphide as usual. In all probability one of these will be sufficiently free from lead to serve as a control solution for the others, thus doing away with the necessity of making controls for each sample. In any case this preliminary experiment will give an idea of the amount of substance suitable for the final test where lead is present.

Notes on the Process.—It is important that in the final match the sodium sulphide solution be added after the lead solution, but it is useful for obtaining a rough indication to add a further quantity of the standard lead solution (up to 0·5 cc. or even more), to the first standard, until a good idea of the requisite amount of lead solution has been obtained; in the final match it is necessary that the whole of the lead solution should be added before the sodium sulphide.

Copper and iron are eliminated by the action of the potassium cyanide, which produces complex cyanides not decomposed by sodium sulphide. Iron sometimes produces a yellow colour with freshly prepared cyanide solution. After standing a day or so this no longer happens.

In the case of certain substances whose solubility in water is not high, it is better to use 5 gm. in the primary solution and 2·5 gm. in the control solution. Acids such as nitric, citric, etc., can be treated in the same way after neutralising with ammonia. Certain oxides and carbonates which are insoluble in water (*e.g.* calcium) are first dissolved in acetic acid, boiled to expel CO_2, made alkaline with ammonia, and treated in the usual way. Certain other substances (*e.g.* cream of tartar, boric acid) are dissolved by the addition of ammonia solution. In all these cases, however, in which the procedure differs from the general method given above, directions will be given in the monograph on the substance in question.

Should the solution of the original substance not be colourless even after filtration, the colour can, if slight, be matched by means of lead sulphide standards before the sodium sulphide is added, and the amount of lead solution so used is deducted from the total amount found in the final comparison. If the colour (which is usually caused by iron salts) is more than can be dealt with in this manner, it may often be prevented by the addition of a little tartaric acid [1] before the cyanide and ammonia.

[1] Teed, *Analyst*, 1892, 17, 142.

When all these measures fail, Harvey and Wilkie [1] recommend the following method: After solution in water, 0·5 cc. of hydrochloric acid (S.G 1·16) are added and 3 cc. of a saturated solution of sodium sulphite, and the solution warmed until the colour due to ferric iron disappears. 3 cc. of the potassium cyanide solution are added, and 6 cc. conc. ammonia solution. The liquid is warmed until colourless, cooled, made up to 150 cc., and the lead estimated in the usual manner. The colour due to excess of iron and the turbidity sometimes noticed when calcium and magnesium salts are examined may be overcome in the absence of copper by carrying out the determination in a solution of known acidity. This can be done [2] by the use of bromophenol blue. The details of this method are as follows: The usual weight of the chemical is dissolved in about 30 cc. water, or just sufficient diluted hydrochloric acid. Two drops of a solution of bromophenol blue are added, and *N*/2 alkali or *N*/2 HCl is run in from a burette until a colourless solution is obtained at the transition point of the indicator. The adjustment is more exact when using *N*/10 acid or alkali at the end. 3 cc. of saturated hydrogen sulphide solution are then added, and the colour matched against a control prepared in the same way, adding the dilute lead solution in the usual way. The dilute lead solution must be brought to the same hydrogen-ion concentration before use, as follows: 5 cc. of the strong lead solution (1 cc.≡0·01 gm. Pb) are diluted to about 450 cc. in a 500 cc. graduated flask, 5 drops of bromophenol blue solution are then added, and *N*/2 alkali run in until the colourless point is reached. The solution is then made up to 500 cc.

In the presence of copper the following method may be used. To the solution of the chemical in water or dilute acid 1 cc. of a 10 per cent. solution of alum (lead free) is added, followed by an excess of ammonia. The precipitated aluminium hydroxide adsorbs the whole of the lead. The liquid is boiled, cooled, and filtered. The residue is then extracted five or six times with 25 cc. of 5 per cent. sulphuric acid and 5 cc. of alcohol, which removes aluminium, copper, and iron. The residue on the filter paper is digested with 50 cc. of hot ammoniacal ammonium acetate, which is poured through the filter three or four times. The filter paper is washed with more ammoniacal ammonium acetate. The filtrate and washings are then tested for lead by the ordinary "alkaline" method, adding 1 cc. of 10 per cent. potassium cyanide solution and sodium sulphide solution. The standards must contain 25 cc. of ammoniacal ammonium acetate. Ammoniacal ammonium acetate is made by neutralising acetic acid with strong ammonia, and adding 50 cc. of strong ammonia for each litre. This method may be used for calcium or barium salts without the addition of alum, dissolving in dilute sulphuric acid, and extracting the residue with dilute sulphuric acid and alcohol as above.

THE DETERMINATION OF COPPER.

It is sometimes necessary to determine the amount of copper present in chemicals, and for that reason an outline is given below of the various methods of estimating copper both when present alone and also when accompanied by iron or lead, or both iron and lead. Minute details of manipulation are not given, but the processes are described at sufficient

[1] *C. & D.*, 1909, 92. [2] Evers, *Y.B.P.*, 1920, 405.

length to enable the worker to carry the processes through. The processes are all colorimetric, and are carried out in Nessler cylinders in a similar manner to the process for lead.

In the Absence of Lead and Iron.—A standard solution of copper sulphate is prepared containing 0·3928 gm. of the crystallised salt per litre. 1 cc. of this solution contains 0·0001 gm. of Cu. The comparison can be carried out either in half per cent. acetic acid solution, using 0·5 cc. of 1 per cent. potassium ferrocyanide, or in slightly alkaline solution using sodium sulphide.

In the Presence of Iron and Absence of Lead.—Copper can be estimated in the same way as lead, using the "acid method" and bromophenol blue.

In the Presence of Iron and Lead.—When both iron and lead are present it is first necessary to determine the lead in the ordinary way. Then copper is estimated by preparing a solution in exactly the same manner but leaving out the potassium cyanide. An amount of lead solution is placed in the standard equivalent to the amount of lead found, and then standard copper solution is added until the coloration produced is a match for the primary solution. The quantity of copper solution added is a measure of the amount of copper in the substance.

If the alum method has to be used for lead determination the copper may be determined in the sulphuric acid-alcohol washings by the "acid method." A small amount may remain in the residue, and this may be determined by comparing the results obtained with and without the addition of potassium cyanide.

In the Presence of Tin.—After determining total metals as "lead" in acid solution with 3 cc. of sulphuretted hydrogen water, 1 cc. of hydrogen peroxide (10 vols.) per 200 cc. of solution is added to a similar quantity and the "lead" again determined. The difference is due to tin.[1]

THE DETERMINATION OF IRON.

Iron is best determined colorimetrically by the red colour produced with potassium thiocyanate.

0·5 gm. of the substance is dissolved in 50 cc. of water in a Nessler cylinder, 5 cc. of dilute HCl (1 : 2), and 5 cc. of 10 per cent. potassium thiocyanate added, and shaken immediately. A standard is prepared with 50 cc. of water, dilute iron solution, and the same quantities of the reagents. The number of cc. of the dilute iron solution added, multiplied by 0·004, gives the percentage of iron.

If a quantity of not more than 0·5 gm. of the substance is used, it is not necessary to use a control containing a smaller quantity of the substance.

The colour must not be matched after standing more than ten minutes, as it fades slightly after that time. The same amount of free hydrochloric acid must be present in each cylinder. The thiocyanate must be added to the iron solution, and not *vice versa*.

The dilute iron solution contains 1 part of Fe in 50,000. It may be prepared by diluting 5 cc. of Liq. Ferri Perchlor. (B.P.) to 250 cc., and then diluting 10 cc. of this to 500 cc. If the iron in the sample is not all in the ferric condition it should be oxidised by adding 2 cc. of nitric acid (yellow,

[1] In the presence of hydrogen peroxide the colour due to lead is destroyed by bright sunlight.

containing nitrous acid), and allowing to stand for two minutes. 2 cc. of 10 vol. hydrogen peroxide solution are then added, and after standing one minute the thiocyanate is added.

The modification of the above thiocyanate method proposed by Marriott and Wolf,[1] which consists in the development of the colour in the presence of acetone, is extremely useful. The colour is intensified and stabilised, and the effect of interfering substances is considerably minimised. The solution to be tested (less than 19 cc.), containing the iron in the ferric condition, is mixed with 1 cc. of strong sulphuric acid, cooled, and mixed with 25 cc. acetone. 5 cc. of 3*M* ammonium thiocyanate are then added and the whole made up to 50 cc. The colour is compared against a standard made in the same way.

[1] *J. Biol. Chem.*, 1906, 1, 456.

SECTION II.

INORGANIC: SYSTEMATIC.

THE following abbreviations, etc., are used in the descriptions which follow. A fuller list will be found in the Appendix.

The figures following the formulæ are the molecular weights of the substances; those in round brackets, the percentage composition, all based upon the International Atomic Weights, 1921 (O = 16).

The solubilities are given in grams of substance per 100 gm. of solvent at a temperature of 15·5° C., except where otherwise stated. The alcohol used is absolute alcohol. The ether is ether of S.G. 0·720, washed with water and dried over calcium chloride.

S.G. . . . Specific Gravity $\frac{15·5° C}{15·5° C}$.
B.Pt. . . . Boiling-point at 760 mm.
M.Pt. . . . Melting-point.
Optical Rotation in degrees per 100 mm. tube.

Aluminium Ammonium Sulphate (Ammonium Alum), $Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ = 906·7. (Al, 5·98; NH_3, 3·76; SO_4, 42·37; H_2O, 47·67.)—Colourless, transparent, crystalline masses. It loses the whole of its water of crystallisation at 100° C., more rapidly at 105 to 110° C. Solubility in water, 12·6; in glycerin, 63; insoluble in alcohol.

Determination of Aluminium.—On 1 gm., as given under Aluminium Potassium Sulphate. Or 1 gm. may be gently ignited to constant weight, when Al_2O_3 remains. $Al_2O_3 \times 8·874 = Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$.

Determination of Ammonia.—On 5 gm., as given under Ammonium Sulphate. 1 cc. N/2 HCl ≡ 0·00851 gm. NH_3 or 0·2267 gm. $Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$.

Determination of Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4 \times 0·9717 = Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$.

Common Impurities.—Copper, calcium, potassium, iron.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the acid method, using 4 gm. and 2 gm. in the control. Limit, 20 parts per million.

Aluminium Chloride, $AlCl_3$=133·4. (Al, 20·30; Cl, 79·70.)—It forms a crystalline hydrate $AlCl_3.6H_2O$ (=241·58; 44·74 per cent. water), which on heating decomposes into water, hydrochloric acid, and alumina. The anhydrous salt is very hygroscopic, and is sometimes used as a desiccating agent. It sublimes without fusing at 183° C. Solubility in water, 41; easily soluble in alcohol or ether.

Determination of Aluminium.—On 0·5 gm., as given under Aluminium Potassium Sulphate. $Al_2O_3 \times 2{\cdot}612 = AlCl_3$; $Al_2O_3 \times 4{\cdot}727 = AlCl_3 . 6H_2O$.

Determination of Chlorine.—On 0·1 gm. by titration, as given under Sodium Chloride. 1 cc. N/10 $AgNO_3 \equiv$ 0·004446 gm. $AlCl_3$ or 0·00805 gm. $AlCl_3.6H_2O$.

Common Impurities.—Copper, calcium, ammonium, potassium, sulphate. Commercial samples have often a yellowish or greenish appearance due to the presence of iron—the pure salt is quite white.

Aluminium Potassium Sulphate (Potassium Alum), $Al_2(SO_4)_3.K_2SO_4.24H_2O$ = 948·8. (Al, 5·71; K, 8·24; SO_4, 40·49; H_2O, 45·56.)—Forms colourless, transparent, crystalline masses. It slowly loses its water of crystallisation at 100° C., much more quickly at 105° to 110° C. Solubility in water, 9·6; in glycerin, 26; insoluble in alcohol.

Determination of Aluminium.—Dissolve 1 gm. with 2 gm. of ammonium chloride in 250 cc. of water; filter if necessary, and add to the filtrate and washings a slight excess of ammonia. Allow to settle, wash by decantation through a filter paper with water containing a little ammonia until free from chloride. Ignite wet until constant in weight. $Al_2O_3 \times 9{\cdot}286 = Al_2(SO_4)_3.K_2SO_4.24H_2O$.

Determination of Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4 \times 1{\cdot}017 = Al_2(SO_4)_3.K_2SO_4.24H_2O$.

Common Impurities.—Copper, calcium, ammonium, iron.

Arsenic.—By the general method on 2 gm. B.P. limit, 5 parts per million.

Lead.—By the acid method, using 4 gm., with 2 gm. in the control. Limit, 20 parts per million.

Modifications and Preparations.—When deprived of its water of crystallisation by heat (below 200° C.) it is known as "Exsiccated Alum" or "Burnt Alum." Except for the absence of water, this should correspond in purity to the hydrated salt. It should be completely (but slowly) soluble in 20 parts of water.

Aluminium Sulphate, $Al_2(SO_4)_3.18H_2O$=666·15. (Al, 8·13; SO_4, 43·23; H_2O, 48·64.)—Colourless, crystalline masses. It should lose the whole of its water of crystallisation below 200° C., forming the anhydrous salt, $Al_2(SO_4)_3$=342·2. Solubility in water, 35; solubility of hydrated salt in water, 26; insoluble in alcohol.

Determination of Aluminium.—On 1 gm., as given under Aluminium Potassium Sulphate. $Al_2O_3 \times 6{\cdot}523 = Al_2(SO_4)_3.18H_2O$. $Al_2O_3 \times 3{\cdot}350 = Al_2(SO_4)_3$.

Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}9524 = Al_2(SO_4)_3.18H_2O$. $BaSO_4 \times 0{\cdot}4892 = Al_2(SO_4)_3$.

Common Impurities.—Lead, copper, calcium, potassium, ammonium, and iron.

Free Acid.—A clear, 10 per cent. solution should not become more than faintly turbid within five minutes on the addition of an equal volume of *N*/10 sodium thiosulphate solution.[1]

Ammonia, NH_3=17·03.

Commercial Ammonia.—Ammonia is placed upon the market as a solution in water of reputed S.G. 0·880, which corresponds to 35·3 per

[1] For a quantitative method, see Beilstein and Grossat, *Z. Anal. Chem.*, 1890, 29, 73; *cf.* Keler and Lunger, *Z. Angew. Chem.*, 1894, 7, 670.

cent. NH_3. Owing to volatilisation it does not remain at this strength above 5° C.

Official Strengths.—*Liquor Ammoniæ Fortis*, B.P., has S.G. 0·888, and contains 32·5 per cent. by weight of NH_3. *Liquor Ammoniæ*, B.P., has S.G. 0·959, and contains 10 per cent. by weight of NH_3. *Aqua Ammoniæ Fortior*, U.S.P., has S.G. about 0·897 at 25° C. and contains 27 to 29 per cent. by weight of NH_3.

Determination.—The strength may be determined from the S.G., using the table of Lunge and Wiernik (Appendix). (Correction for 1° C.=0·00063.) Or, by titration with $N/2$ hydrochloric acid to methyl red. 1 cc. $N/2$ HCl ≡ 0·00851 gm. NH_3. The titration is best carried out by weighing 5 cc. of water in a weighing bottle, adding about 2 cc. of the sample and weighing again, finally washing the contents into a beaker for the titration.

Common Impurities.—Lead, iron, zinc, calcium, sulphates, chlorides, and carbonates.

Non-volatile Matter.—10 cc. evaporated on the water bath should leave less than 1 mg. of residue.

Carbonates.—The addition of 10 cc. of lime water to 5 cc. of ammonia should cause no precipitate, even on boiling.

Tarry Matters.—10 cc. diluted with water and made slightly acid with sulphuric acid should not change colour and should be free from unpleasant smell. The resulting solution evaporated to dryness on the water bath should leave a perfectly white residue, entirely volatile on ignition.

Permanganate Test.—5 cc., made slightly acid with sulphuric acid, should not discharge the colour of 2 drops of $N/10$ potassium permanganate solution in five minutes.

Arsenic.—Evaporate 20 gm. on the water bath to about 5 cc. Add 40 cc. of water and 15 cc. of brominated hydrochloric acid; decolorise with stannous chloride solution drop by drop and proceed as usual. For the electrolytic method, 35 cc. of cadmiumated sulphuric acid are added to the residue. Limit, 0·5 parts per million.

Lead.—50 cc. should give no colour with 3 drops of sodium sulphide solution.

Ammonium Acetate, $CH_3.COONH_4$=77·07. (NH_3, 22·10; $CH_3.COOH$, 77·90.)—M.Pt., 89° C. Very soluble in water and alcohol.

Determination of Ammonia.—On 1 gm., as given under Ammonium Sulphate. 1 cc. $N/2$ HCl ≡ 0·03853 gm. $CH_3.COONH_4$.

Acetate.—1 gm. is boiled with 30 cc. of $N/2$ NaOH until all the ammonia is driven off, and then titrated back with $N/2$ HCl to phenolphthalein and the solution evaporated to dryness. The acetate may then be determined as under Potassium Acetate. 1 cc. $N/2$ HCl ≡ 0·03853 gm. $CH_3.COONH_4$.

Common Impurities.—Copper, iron, calcium, sulphate, sulphite, carbonate, chloride, and tarry matter.

Non-volatile Matter.—No residue should be left on ignition.

Lead and Copper.—2 gm. dissolved in 50 cc. water should give no coloration with sulphuretted hydrogen water.

Ammonium Benzoate, $C_6H_5.COONH_4$=139·1. (NH_3, 12·24; $C_6H_5.COOH$, 87·76.) Solubility in water, 17; in alcohol, 1·5; in glycerin, 12.

Determination of Ammonia.—On 1 gm., as under Ammonium Sulphate. 1 cc. $N/2$ HCl ≡ 0·0695 gm. $C_6H_5COONH_4$.

Determination of Benzoic Acid.—Dissolve 1·5 gm. in 25 cc. of water, add 25 cc. of *N*/2 HCl and extract three times with 20 cc. of ether. Wash the mixed ethereal washings with 5 cc. of water and titrate the mixed aqueous liquids with *N*/2 NaOH to methyl red. 1 cc. *N*/2 HCl ≡ 0·0695 gm. $C_6H_5COONH_4$. The ethereal solution may be evaporated at a low temperature (below 60° C.) in a tared dish and dried to constant weight in the desiccator. The benzoic acid thus obtained may be titrated with *N*/2 NaOH to phenolphthalein or thymol blue. 1 cc. *N*/2 NaOH ≡ 0·061 gm. C_6H_5COOH or 0·0695 gm. $C_6H_5COONH_4$.

Common Impurities.—Chloride, sulphate, and tarry matter.

Non-volatile Matter.—No residue should be left on ignition.

Arsenic.—Mix 5 gm. into a paste with 2 gm. of calcium hydroxide and 5 cc. of water, dry, and gently ignite. Dissolve the residue in 16 cc. of brominated hydrochloric acid and 45 cc. of water, and remove the excess of bromine by means of a few drops of stannous chloride solution. Continue the test in the usual manner. Limit, 2 parts per million. 5 gm. may be treated directly by the electrolytic method.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Ammonium Bromide, NH_4Br=97·96. (NH_3, 17·39 ; Br, 81·55.) Solubility in water, 72 ; in alcohol, 3.

Determination of Ammonia.—On 1 gm., as under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·04898 gm. NH_4Br.

Bromine.—Dissolve 0·4 gm. in 25 cc. of water, add 50 cc. of *N*/10 silver nitrate and 2 cc. of ferric alum solution ; titrate back with *N*/10 thiocyanate until red. 1 cc. *N*/10 $AgNO_3$ ≡ 0·009796 gm. NH_4Br. Bromine may also be determined gravimetrically on 0·5 gm. AgBr × 0·5216 = NH_4Br.

Common Impurities.—Chloride, iodide, bromate, nitrate, sulphate, iron, and barium.

Bromate.—The salt should not assume an immediate yellow colour with dilute sulphuric acid.

Iodide —A solution should not develop an immediate blue colour when treated with a drop of bromine water and a little starch paste.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. For the electrolytic method, 2 gm. should be evaporated with 2 cc. of sulphuric acid before electrolysing.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Ammonium Carbonate.—The ammonium carbonate of commerce is a mixture of ammonium hydrogen carbonate NH_4HCO_3 (79·05) and ammonium carbamate $CO.NH_2.O.NH_4$ (78·07).—In testing this article the external effloresced portion should be removed before taking a sample. Solubility in water, 25 ; in alcohol, 0·5 ; in glycerin, 20.

Determination.—Add 50 cc. of *N*/2 hydrochloric acid to 1 gm. of the salt, and titrate back with *N*/2 sodium hydroxide to bromophenol blue until blue. 1 cc. *N*/2 HCl ≡ 0·00851 gm. NH_3. About 31 per cent. of NH_3 should be found.

Common Impurities.—Copper, iron, chloride, sulphate.

Tar Bases.—May be tested for as under Ammonia.

Thiocyanates.—1 gm. dissolved in water should not give a colour with 1 drop of solution of ferric chloride.

Arsenic.—Dissolve 5 gm. in water, and boil until most of the ammonium carbonate has volatilised. Add 15 cc. of brominated hydrochloric acid, and then add stannous chloride solution drop by drop until colourless. Proceed as usual. Limit, 2 parts per million. 5 gm. may be treated directly with 35 cc. of cadmiumated sulphuric acid for the electrolytic method.

Lead.—Use 7 gm. in the primary solution and 2 gm. in the control. Acidify and boil off carbon dioxide. Final comparison may be carried out in acid or alkaline solution. Limit, 5 parts per million.

B.P. Requirements.—1 gm. shall require not less than 18 cc. of *N* HCl, which is equivalent to 30·67 per cent. of NH_3.

Ammonium Chloride. NH_4Cl=53·50.—Ammonium chloride occurs in the form of small, colourless crystals. (NH_3, 31·64; Cl, 66·28.) Solubility in water, 35·2; in alcohol, 0·6.

Determination of Ammonia.—On 0·5 gm., as under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·02675 gm. NH_4Cl.

Chloride.—On 0·2 gm., as given under Sodium Chloride. 1 cc. *N*/10 $AgNO_3$ ≡ 0·00535 gm. NH_4Cl. AgCl × 0·3736 = NH_4Cl.

Common Impurities.—Copper, iron, calcium, thiocyanate, carbonate, and sulphate.

Non-volatile Matter.—5 gm. evaporated on the water bath with nitric acid should leave a white residue completely volatile on ignition.

Thiocyanate.—Two drops of ferric chloride solution added to 2·5 gm. dissolved in 50 cc. of water should give no red colour.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method with 12 gm. in the primary solution and 2 gm. in the control. Limit, 5 parts per million.

Commercial varieties of ammonium chloride are the "lump" and "tooth crystals" or "battery crystals."

Ammonium Citrate, $C_3H_4OH.(COONH_4)_3.H_2O$=261·2. ($NH_3$, 19·56; $C_3H_4OH(COOH)_3$, 73·54; H_2O, 6·90.)—The crystals are very deliquescent, and tend to lose ammonia on exposure to air. Very soluble in water.

Determination of Ammonia.—On 0·8 gm., as under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·04354 gm. $C_3H_4OH(COONH_4)_3.H_2O$, or 0·040538 gm. $C_3H_4OH(COONH_4)_3$.

Citrate.—On 1 gm., as under Ammonium Acetate. 1 cc. *N*/2 HCl ≡ 0·04354 gm. $C_3H_4OH(COONH_4)_3.H_2O$, or 0·040538 gm. $C_3H_4OH.(COONH_4)_3$.

Common Impurities.—Copper, iron, sulphate.

Non-volatile Residue.—The residue on ignition should not exceed 0·01 per cent., and should be white.

Tartrates.—Ammonium citrate should not respond to the test for tartrates given under citric acid.

Arsenic.—By the general method, using 5 gm.

Lead.—By the general method.

Ammonium Hippurate, $C_6H_5CONHCH_2.COONH_4$ = 196·1. ($C_6H_5CONHCH_2.COOH$, 91·33; NH_3, 8·67.)—The commercial salt usually contains an indefinite amount of free hippuric acid. The neutral salt is very soluble in water, 166.

Determination of Ammonia.—2 gm. are distilled with excess of sodium hydroxide into 25 cc. of *N*/2 HCl in the usual way. 1 cc. *N*/2 HCl ≡ 0·09805 gm. ammonium hippurate.

Hippuric acid.—0·4 gm. is dissolved in 20 cc. of water, 2 drops of phenolphthalein added, and solution of ammonia drop by drop until the solution is alkaline. 20 cc. of formaldehyde solution (20 per cent. H.CHO), followed by 20 cc. of *N*/5 NaOH solution, are then added, and the excess of alkali titrated with *N*/10 HCl. A blank titration is carried out with *N*/10 HCl against 20 cc. of water made just alkaline with a drop of ammonia solution, 2 drops of phenolphthalein solution, 20 cc. of formaldehyde solution, and 20 cc. of *N*/5 NaOH. 1 cc. *N*/10 NaOH ≡ 0·01791 gm. hippuric acid.

Ammonium Ichthosulphonate or **Sulphicthyolate** ("Ichthyol").—A dark brown, viscous liquid containing the ammonium salts of the sulphonic acids prepared from ichthyol, an oil obtained by distilling a bituminous schist occurring in the Tyrol. Various substitutes with similar properties are also on the market prepared from oils obtained from other sources. The natural substance has the following average composition. Total sulphur, 11·0 per cent.; sulphonic sulphur, 2·6 per cent.; total ammonia, 3·0 per cent.; ammonium sulphate, 6·0 per cent. It is soluble in water, and almost entirely soluble in a mixture of equal parts of alcohol and ether. The ash should not exceed 0·2 per cent.

Determination of Total Ammonia.—Distil 1 gm. with excess of potassium hydroxide in the usual way. 1 cc. N/10 HCl ≡ 0·001703 gm. NH_3.

Ammonium Sulphate.—Dissolve 5 gm. in 50 cc. of water, add 10 cc. of 10 per cent. albumen solution, followed by 5 portions of 5 cc. of dilute hydrochloric acid, shaking the solution after each addition. Dilute to about 350 cc., filter, and determine sulphate in the filtrate as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}566 = (NH_4)_2SO_4$. $BaSO_4 \times 0{\cdot}1373 = S$.

Total Sulphur.—Weigh 1 gm. into a Kjeldahl flask, add 30 cc. of water, 5 gm. of potassium chlorate, and 30 cc. of nitric acid, and evaporate to about 5 cc. Add two lots of 25 cc. of hydrochloric acid, and evaporate to about 5 cc. after each addition. Dilute to 100 cc., and determine the sulphate as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}1373 = S$.

"*Sulphonic*" and "*Organic*" *Sulphur.*—Subtract the ammonia in the ammonium sulphate [$(NH_4)_2SO_4 \times 0{\cdot}2575 = NH_3$] from the total ammonia; the result, multiplied by 1·88, represents the sulphur as sulphonic acids (combined with a portion of the ammonia). The sum of the "sulphonic" sulphur and the "sulphate" sulphur subtracted from the total sulphur will give the "organic" sulphur.

Ammonium Iodide, NH_4I=145·0. (NH_3, 11·75; I, 87·55.)—A white, crystalline, deliquescent solid. Solubility in water, 167; in alcohol, 26; in glycerin, 75.

Determination of Ammonia.—On 1·5 gm., as under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·0725 gm. NH_4I.

Iodide.—On 0·5 gm., as under Ammonium Bromide. 1 cc. *N*/10 $AgNO_3$ ≡ 0·0145 gm. NH_4I, or gravimetrically, $AgI \times 0{\cdot}6174 = NH_4I$.

Common Impurities.—Iron, barium, chlorides, bromides, sulphates, and thiocyanates.

Chloride and *Bromide.*—Indicated by the silver titration, showing more than 100 per cent. of ammonium iodide. The salt should not have more than the faintest yellow colour.

Free Iodine.—20 cc. of a 1 per cent. solution shaken with 1 cc. of chloroform should not impart to the latter a violet colour.

Arsenic.—By the general method on 2 gm.; limit, 5 parts per million.

For the electrolytic method 2 gm. should be warmed with 2 cc. of sulphuric acid until hydriodic acid and iodine are removed, before carrying out the test.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Ammonium Molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$=1236·3. (NH_3, 8·76; MoO_3, 81·53; H_2O, 5·83.)—Colourless or faintly green, dense, crystalline masses. Solubility in water, 40.

Determination of Ammonia.—On 2·2 gm., as under Ammonium Sulphate. 1 cc. N/2 HCl ≡ 0·1030 gm. $(NH_4)_6.Mo_7O_{24}.4H_2O$.

Molybdic Anhydride.—Carefully ignite about 1 gm. and weigh the molybdic anhydride remaining. *Cf.* Molybdic Acid (p. 88), $MoO_3 \times 1{\cdot}227 = (NH_4)_6.Mo_7O_{24}.4H_2O$.

Common Impurities.—Heavy metals, phosphate, chloride, sulphate.

Phosphates.—1 gm. should give a clear solution with 25 cc. of water and 1·5 cc. of ammonia. This solution poured into 15 cc. of 25 per cent. nitric acid should not show any yellow precipitate after standing for two hours in a warm place.

Heavy Metals.—1 gm. in 10 cc. of water made alkaline with ammonia should not show any darkening with a few drops of sodium sulphide solution.

Ammonium Nitrate, NH_4NO_3=80·05. (NH_3, 21·28; NO_3, 77·46.)—Colourless crystals. Solubility in water, 180; in alcohol, 2·4.

Determination of Ammonia.—On 1·0 gm., as given under Ammonium Sulphate, 1 cc. *N*/2 HCl ≡ 0·04003 gm. NH_4NO_3.

Nitrate.—If necessary, this may be determined on 0·5 gm. as under Potassium Nitrate.

Common Impurities.—Copper, iron, calcium, carbonate, phosphate, thiocyanate, sulphate, and chloride.

Non-volatile Residue.—Less than 0·01 per cent. on careful ignition.

Nitrites.—1 gm. dissolved in 20 cc. of water acidulated with sulphuric acid should give no yellow colour on adding 1 cc. of a 0·5 per cent. solution of metaphenylenediamine hydrochloride, and standing for ten minutes.

Arsenic.—Heat 2 gm. with 2 cc. of sulphuric acid and 5 cc. of water until white fumes are evolved; cool, add 3 cc. of water, and again heat until white fumes are evolved. Add 50 cc. of hot water and 10 cc. of stannated hydrochloric acid, and proceed as usual. Limit, 5 parts per million.

Lead.—By the general method on 12 gm. with 2 gm. in the control. Limit, 10 parts per million.

Ammonium Oxalate, $(COONH_4)_2.H_2O$=142·1. (NH_3, 23·97; $H_2C_2O_4$, 63·38; H_2O, 12·65.)—A white, crystalline solid. Solubility in water, 4·2.

Determination of Ammonia.—On 0·8 gm., as given under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·03553 gm. $(COONH_4)_2.H_2O$.

Oxalate.—Dissolve 0·4 gm. in about 100 cc. of hot water containing about 5 cc. of conc. sulphuric acid and titrate with *N*/10 permanganate until just pink. 1 cc. *N*/10 $KMnO_4$ ≡ 0·007105 gm. $(COONH_4)_2.H_2O$.

Common Impurities.—Iron, chloride, sulphate.

Non-volatile Residue.—The residue on gentle ignition should not exceed 0·1 per cent.

Insoluble Impurities.—A solution of 1 gm. in 50 cc. of water should be absolutely bright.

Heavy Metals.—50 cc. of a 2 per cent. solution should show no darkening on the addition of 1 cc. of ammonia and 2 drops of sodium sulphide.

Ammonium Persulphate, $(NH_4)_2S_2O_8$=228·2. (NH_3, 14·93.)—A white, crystalline powder which is hydrolysed on boiling with water with formation of free sulphuric acid and evolution of oxygen. $(NH_4)_2S_2O_8+H_2O=(NH_4)_2SO_4+H_2SO_4+O$. It should contain about 95 per cent. of $(NH_4)_2S_2O_8$. Solubility in water, 59; insoluble in alcohol.

Determination of Ammonia.—On 1·5 gm., as given under Ammonium Sulphate. 1 cc. $N/2$ HCl ≡0·05705 gm. $(NH_4)_2S_2O_8$.

Persulphate.—Place 0·5 gm. in a 400 cc. flask and add $N/10$ oxalic acid and a solution of 0·2 gm. of silver sulphate in 20 cc. of dilute sulphuric acid. Heat the mixture on the water bath until no more carbon dioxide is evolved (15 to 20 minutes), and dilute to about 100 cc. with warm water. Titrate the excess of oxalic acid with $N/10$ permanganate. 1 cc. $N/10$ $H_2C_2O_4 \equiv$ 0·01141 gm. $(NH_4)_2S_2O_8$. As an alternative method boil 2 gm. with about 100 cc. of water for 20 minutes, cool, and titrate the sulphuric acid formed with $N/2$ sodium hydroxide to methyl red. 1 cc. $N/2$ NaOH ≡0·05705 gm. $(NH_4)_2S_2O_8$.

Other Tests.—The residue on gentle ignition should not exceed 0·1 per cent. The salt should be practically free from chloride.

Ammonium Phosphate, $(NH_4)_2HPO_4$=132·1. (NH_3, 25·78; H_3PO_4, 74·22.)—A white, crystalline solid. Solubility in water, 131; insoluble in alcohol.

Determination of Ammonia.—On 0·8 gm., as given under Ammonium Sulphate. 1 cc. $N/2$ HCl ≡ 0·03303 gm. $(NH_4)_2HPO_4$.

Phosphate.—On 0·5 gm., as given under Sodium Phosphate. $Mg_2P_2O_7 \times$ 1·187=$(NH_4)_2HPO_4$.

Common Impurities.—Copper, iron, sulphate, chloride.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 7 gm., with 2 gm. in the control. Limit, 10 parts per million.

Ammonium Salicylate, $C_6H_4.OH.COONH_4$=155·1. (NH_3, 10·98; $C_6H_4OH.COOH$, 89·02).—Solubility in water, 100; in alcohol, 35.

Determination of Ammonia.—On 1·5 gm., as given under Ammonium Sulphate. 1 cc. $N/2$ HCl ≡0·0775 gm. $C_6H_4OH.COONH_4$.

Salicylic Acid.—On 1·5 gm., as given under Ammonium Benzoate. 1 cc. $N/2$ NaOH ≡0·0775 gm. $C_6H_4.OH.COONH_4$. $C_6H_4.OH.COOH \times$ 1·1234=$C_6H_4.OH.COONH_4$.

Non-volatile Matter.—The salt should be completely volatile on careful ignition (Ash, 0·1 per cent., U.S.P.).

Arsenic.—Mix 2 gm. into a paste with 1 gm. of lime and 5 cc. of water, dry on the water bath, and ignite gently. Dissolve the residue in a mixture of 15 cc. of brominated hydrochloric acid and 50 cc. of water; remove excess of bromine with a few drops of stannous chloride solution, and proceed as usual. Limit, 5 parts per million.

Lead.—2 gm. in 50 cc. of water should show no appreciable darkening with 2 drops of sodium sulphide solution.

Ammonium Sulphate, $(NH_4)_2SO_4$=132·1. (NH_3, 25·75; SO_4, 72·70.)—Solubility in water, 74; insoluble in alcohol.

Determination of Ammonia.—Weigh 0·7 gm. into a large, flat-bottomed flask (1 to 2 litres), attached by means of a spray trap to a condenser, to

the lower end of which is fitted a 500 cc. extraction flask carrying an exit tube filled with glass beads. Run 25 cc. of *N*/2 hydrochloric acid through the beads into the flask, and then add an excess of sodium hydroxide solution to the boiling contents of the flask, and distil about 400 cc. Titrate back with *N*/2 sodium hydroxide solution to methyl red. 1 cc. *N*/2 HCl ≡ 0·03302 gm. $(NH_4)_2SO_4$ ≡ 0·008515 gm. NH_3.

Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}5661 = (NH_4)_2SO_4$.

Common Impurities.—Copper, iron, chloride, nitrate, and thiocyanate.

Non-volatile Residue.—The salt should be completely volatile on careful ignition.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 12 gm. with 2 gm. in the control. Limit, 10 parts per million.

Ammonium Thiocyanate, NH_4SCN=76·1. (NH_3, 23·38.)—Colourless, deliquescent plates. Solubility in water, 150; very soluble in alcohol.

Determination of Ammonia.—On 1 gm., as given under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·03806 gm. NH_4SCN.

Thiocyanate.—Dissolve 0·7 gm. in water, and make up to 100 cc. With this solution in the burette, titrate 25 cc. of *N*/10 silver nitrate, using 5 cc. of ferric alum solution as indicator, the first tinge of a permanent red colour being taken as the end point. 25 cc. *N*/10 $AgNO_3$ ≡ 0·1903 gm. NH_4SCN, or 1 cc. ≡ 0·00761 gm.

Common Impurities.—The salt should leave no residue on ignition, and should be entirely soluble in ten volumes of alcohol. It should be free from sulphate.

Iron.—A 10 per cent. solution should remain colourless on the addition of a few drops of hydrochloric acid. Iron is often indicated by a pinkish tint in the salt.

Heavy Metals.—No darkening should take place on the addition of 2 drops of sodium sulphide to 50 cc. of a 5 per cent. solution.

Ammonium Valerianate or Valerate, $C_4H_9.COONH_4$=119·1. (NH_3, 14·30; C_4H_9COOH, 85·70.)—The commercial salt contains only about 35 per cent. of ammonium valerate with 65 per cent. of free valeric acid. Solubility in water, 330; in alcohol, 100; soluble in ether.

Determination of Ammonia.—On 1·5 gm., as under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·00852 gm. NH_3, or 0·0595 gm. $C_4H_9.COONH_4$.

Valeric Acid.—Weigh out 0·2 gm., add 25 cc. of *N*/10 sulphuric acid, make up to 100 cc., and distil 90 cc. Titrate the distillate with *N*/10 NaOH to thymol blue. 1 cc. *N*/10 NaOH ≡ 0·01191 gm. $C_4H_9.COONH_4$.

Free Valeric Acid.—Titrate 1 gm. with *N*/10 NaOH to thymol blue. 1 cc. *N*/10 NaOH ≡ 0·0102 gm. C_4H_9COOH. The ash should not exceed 0·05 per cent.

Acetate.—The filtrate produced after precipitating 0·5 gm. from aqueous solution with slight excess of ferric chloride solution should not possess a deep red colour.

Heavy Metals.—2 gm. dissolved in water, acidulated with dilute sulphuric acid and filtered from the precipitated valeric acid, should show no darkening with sulphuretted hydrogen solution.

Antimonious Oxide, Sb_2O_3=288·4. (Sb, 83·36; O, 16·64.)—A greyish-white powder which sublimes at a bright red heat. Insoluble in water,

alcohol, and nitric acid; soluble in hydrochloric and tartaric acids, and in potassium bitartrate.

Determination.—Dissolve 0·25 gm. in dilute hydrochloric acid, add 5 gm. of Rochelle salt and a slight excess of sodium bicarbonate and titrate with $N/10$ iodine. 1 cc. $N/10$ I ≡ 0·00721 gm. Sb_2O_3.

Common Impurities.—Iron, calcium, potassium, chloride, and sulphate.

Antimonic Oxide.—The oxide should be completely soluble in an aqueous solution of potassium bitartrate.

Arsenic.—Dissolve 2 gm. in 5 cc. of pure hydrochloric acid. Add 5 cc. of stannous chloride solution and heat for fifteen minutes on the water bath. No darkening should develop after standing one hour.

Antimony Potassium Tartrate (*Antimonium Tartaratum*—Tartar Emetic) $(KSbOC_4H_4O_6)_2.H_2O$=664·7. (K, 11·76; Sb, 36·17; $C_4H_4O_6$, 44·54; H_2O, 2·71.)—Solubility in water, 5·9; insoluble in alcohol.

Determination.—Dissolve 0·5 gm. in 30 cc. of water, add 25 cc. of a cold, saturated solution of sodium bicarbonate, and titrate with $N/10$ iodine to starch. 1 cc. $N/10$ I ≡ 0·01662 gm. $(KSbOC_4H_4O_6)_2.H_2O$.

Common Impurities.—Lead, copper, iron, calcium, ammonia, chloride, and sulphate.

Free Acid.—2 gm. should give no effervescence with a saturated solution of sodium bicarbonate.

Arsenic.—Determined as under Antimonious Oxide.

Antimonious Sulphide, Sb_2S_3=333·6. (Sb, 71·42; S, 28·58.)—Insoluble in water; soluble in strong hydrochloric acid, leaving not more than 1 per cent. residue.

Determination of Antimony.—Dissolve 0·3 gm. in strong hydrochloric acid, dilute with five times its bulk of water and add 5 gm. of Rochelle salt, slight excess of sodium bicarbonate, and titrate with $N/10$ iodine. 1 cc. $N/10$ I ≡ 0·008415 gm. Sb_2S_3.

Sulphur.—Dissolve 0·2 gm. in fuming nitric acid to which a little bromine has been added, and warm gently until all the sulphur is oxidised. Remove the excess of bromine by boiling, dilute with water, filter, and precipitate the sulphate with barium chloride, as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}1373 = S$; $BaSO_4 \times 0{\cdot}4804 = Sb_2S_3$.

Arsenic.—Dissolve 1 gm. in 10 cc. of hydrochloric acid and 5 cc. of water with a little potassium chlorate. Filter, evaporate to 3 cc. and heat for fifteen minutes in the boiling water bath with an equal volume of stannous chloride solution. No darkening should develop on standing one hour.

Antimony, Sulphurated.—A product containing antimony sulphide, antimony oxides, and free sulphur, obtained by treating antimony sulphide with sulphur and caustic soda, and precipitating with sulphuric acid. Insoluble in water, but soluble in caustic soda solution and in hydrochloric acid—in the latter with evolution of sulphuretted hydrogen and liberation of free sulphur.

Determination.—On 0·2 gm., as given under Antimony Sulphide.[1]

The B.P. requires that 3 gm., moistened with nitric acid, warmed with successive portions of fuming nitric acid until red fumes cease to be evolved, and then dried and carefully heated to redness, shall leave a whitish residue weighing from 1·6 to 1·8 gm.

Common Impurities.—Silicious matter, chloride, and sulphate.

[1] *Cf.* F. H. Alcock, *Pharm. J.*, 1913, **37**, 213, and *Y.B.P.*, 1909, 297, 299.

Arsenic.—Dissolve 0·01 gm. by boiling in a small flask with 0·2 gm. of calcium hydroxide and 5 cc. of water, adding 2 cc. of bromine solution, boiling gently, and then adding 17 cc. of hydrochloric acid and 5 cc. of water, and continuing the boiling until most of the bromine is volatilised, the last traces being removed by adding a slight excess of stannous chloride solution. Connect the flask to a condenser and distil 20 cc. Wash the condenser and flask and return the distillate to the flask. Add a drop of stannous chloride solution and redistil 16 cc. Add 45 cc. of water to the distillate, together with a few drops of stannous chloride solution and proceed as usual. Limit, 0·1 per cent.

Arsenious Iodide, AsI_3=455·7. (As, 16·45; I, 83·55.)—An orange-red, crystalline powder which should give an almost colourless solution with water. It is decomposed by water forming hydriodic and arsenious acids. Solubility in water, 6; in alcohol, 2·2; in carbon bisulphide, 5·3.

Determination of Arsenic.—Dissolve 0·5 gm. in 50 cc. of water, add about 2 gm. of sodium bicarbonate, and titrate with *N*/10 iodine. 1 cc. *N*/10 I ≡ 0·02279 gm. AsI_3.

Iodide.—Dissolve 0·5 gm. in 50 cc. of water, add 3 cc. of conc. nitric acid and 50 cc. of *N*/10 silver nitrate, and titrate back with *N*/10 thiocyanate to ferric alum. 1 cc. *N*/10 $AgNO_3$ ≡ 0·01519 gm. AsI_3.

Ash.—No loss of iodine should occur at 100° C., but at higher temperatures the iodide should be completely volatile (99·5 per cent. volatile matter, U.S.P.).

Arsenious Oxide (Arsenic Trioxide, Arsenious Acid), As_2O_3=197·9. (As, 75·75; O, 24·25.)—Solubility in water, 1·65 (crystalline); 3·57 (amorphous); in alcohol, 0·4; in glycerin, 12. It should be completely soluble in ammonia.

Determination.—Dissolve 0·15 gm. in boiling water by the addition of sodium hydroxide drop by drop. Neutralise to phenolphthalein with dilute hydrochloric acid, cool, and dissolve 2 gm. of sodium bicarbonate in the solution. Titrate with *N*/10 iodine solution. 1 cc. *N*/10 I ≡ 0·004948 gm. As_2O_3.

Ash.—The oxide should be entirely volatile on careful ignition (in the fume chamber).

Heavy Metals.—About 0·15 gm. dissolved in water acidified with hydrochloric acid should give, on passing sulphuretted hydrogen, a light yellow precipitate entirely soluble in ammonium carbonate solution, showing absence of antimony, cadmium, lead, and tin. The solution in ammonia should not assume a yellow colour on acidification with hydrochloric acid, showing absence of arsenious sulphide.

Barium Carbonate, $BaCO_3$=197·4. (Ba, 69·60; CO_2, 22·29; CO_3, 30·40.)—Insoluble in water; soluble in dilute hydrochloric acid to a clear, colourless solution.

Determination of Barium.—On 0·3 gm. after solution in dilute hydrochloric acid, as given under Barium Chloride. $BaSO_4 \times 0{\cdot}846 = BaCO_3$.

Carbonate.—On 0·3 gm., as given under Calcium Carbonate. $CO_2 \times 4{\cdot}486 = BaCO_3$.

Ammonium Salts.—1 gm. shaken with 5 cc. of water and boiled with 40 per cent. sodium hydroxide solution should not evolve any ammonia.

Sulphide.—1 gm. boiled in a tube with dilute hydrochloric acid should give no stain on lead acetate paper.

Heavy Metals.—2 gm., dissolved in hydrochloric acid, the carbon dioxide boiled off, and then made alkaline with ammonia, should show no darkening with sodium sulphide solution.

Alkali Metals.—As under Barium Chloride.

Arsenic.—Dissolve 2 gm. in 12 cc. of brominated hydrochloric acid and add 50 cc. of water. Remove the excess of bromine by adding stannous chloride solution drop by drop, and proceed as usual.

Barium Chloride, $BaCl_2 . 2H_2O$=244·3. (Ba, 56·22; Cl, 29·03; H_2O, 14·75.)—The salt loses its water of crystallisation at 100° C. Solubility in water, 37; insoluble in alcohol.

Determination of Barium.—Dissolve 0·3 gm. in about 200 cc. of water and add 10 cc. of conc. hydrochloric acid. Heat to boiling, and when boiling add 20 cc. of a boiling 10 per cent. sulphuric acid solution, drop by drop, with thorough agitation. Allow to stand for several hours in a warm place, filter, wash by decantation, and filter through a Gooch crucible. Wash thoroughly with hot water, dry in the oven, and weigh. $BaSO_4 \times 0·8923 = BaCl_2$; $BaSO_4 \times 1·047 = BaCl_2.2H_2O$.

Chloride.—Dissolve 0·5 gm. in 50 cc. of water, pipette in 50 cc. of *N*/10 silver nitrate solution, and titrate back with *N*/10 thiocyanate, using ferric alum as indicator. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·01222 gm. $BaCl_2.2H_2O$, or 0·0104 gm. $BaCl_2$.

Common Impurities.—Copper, iron, arsenic, lead, nitrate, and sulphate, the absence of the last being shown by the aqueous solution being quite bright.

Alkali Metals.—Dissolve 2 gm. in 50 to 100 cc. of water containing 2 cc. of conc. hydrochloric acid, boil, add 10 cc. of 10 per cent. sulphuric acid, and allow to stand for some hours. Filter, evaporate the filtrate to dryness, and ignite. Not more than 1 mgm. of residue should be obtained.

Strontium and Calcium.—The salt should be insoluble in alcohol and the alcoholic menstruum should burn with a flame free from red tinge.

Heavy Metals.—Dissolve 2·5 gm. in 50 cc. of water, and add 2 drops of sodium sulphide solution. No darkening should take place.

Barium Hydroxide, $Ba(OH)_2.8H_2O$=315·5. (Ba, 43·54; OH, 10·78; H_2O, 45·68.)—Solubility in water, 6.

Determination of Barium.—On 0·3 gm., as given under Barium Chloride. $BaSO_4 \times 0·734 = Ba(OH)_2$; $BaSO_4 \times 1·352 = Ba(OH)_2.8H_2O$.

Alkalinity.—Dissolve 2 gm. in 100 cc. of water free from carbon dioxide, filter rapidly, and wash with water free from carbon dioxide. Titrate the filtrate with *N*/2 HCl to phenolphthalein. 1 cc. *N*/2 HCl $\equiv$ 0·07888 gm. $Ba(OH)_2.8H_2O$, or 0·04285 gm. $Ba(OH)_2$.

Common Impurities.—Calcium, sulphate, chloride, carbonate, sulphide.

Calcium.—As under Barium Chloride.

Alkali Metals.—As under Barium Chloride.

Sulphide.—As under Barium Carbonate.

Barium Hypophosphite, $Ba(H_2PO_2)_2$=267·5. (Ba, 51·36; H_2PO_2, 48·64.) —Solubility in water, 28.

Determination of Barium.—On 0·3 gm., as under Barium Chloride, $BaSO_4 \times 1·146 = Ba(H_2PO_2)_2$.

Hypophosphite.—Dissolve 5 gm. in 80 cc. of water, add 10 cc. of lead acetate solution, and make up to 100 cc. Shake and allow to stand for one hour. Pipette off 10 cc. of the clear liquid and add 50 cc. of *N* $K_2Cr_2O_7$

and 10 cc. of conc. sulphuric acid, and heat on the water bath for one hour. Cool, and make up to 250 cc. Take 25 cc. of this latter solution (equivalent to 0·05 gm. of the salt), add 2 gm. of potassium iodide, and titrate the liberated iodine with *N*/10 thiosulphate. A blank experiment, omitting the hypophosphite, should be carried out at the same time. 1 cc. *N* $K_2Cr_2O_7 \equiv$ 0·03344 gm. $Ba(H_2PO_2)_2$.

Common Impurities.—Copper, iron, magnesium, chloride, sulphate, and phosphate.

Arsenic.—Mix 2 gm. with 2 gm. of potassium chlorate, add 18 cc. of hydrochloric acid, and allow to stand for an hour. Warm to expel chlorine, transfer to a distilling flask, add 1 cc. of stannous chloride solution, and distil 15 cc.; add 40 cc. of water to the distillate and 3 drops of stannous chloride solution. Proceed as usual. Limit, 5 parts per million.

Lead.—By the acid method on 4 gm. with 2 gm. in the control, solution being effected with acetic acid. Limit, 10 parts per million (*cf.* Calcium Hypophosphite, p. 60).

Barium Nitrate, $Ba(NO_3)_2$=261·4. (Ba, 52·55; NO_3, 47·45.)—Solubility in water, 7·71; insoluble in alcohol.

Determination of Barium.—On 0·3 gm., as under Barium Chloride. $BaSO_4 \times 1{\cdot}120 = Ba(NO_3)_2$.

Nitrate.—As under Potassium Nitrate.

Common Impurities.—Sulphate, chloride, iron.

Alkali Metals.—As under Barium Chloride.

Heavy Metals.—A solution of 1 gm. in 50 cc. of water should show no darkening on the addition of 2 drops of solution of sodium sulphide.

Barium Sulphate, $BaSO_4$=233·4. (Ba, 58·85; SO_4, 41·15.)—It is used in large doses in order to define the alimentary tract for X-ray examination. For this purpose it is of the utmost importance that it should be free from soluble barium salts and other impurities. It should be as light as possible. 10 gm. should occupy not less than 6 cc.

Soluble Barium Salts.[1]—Heat 10 gm. on the water bath with 100 cc. of *N*/10 hydrochloric acid. Filter and treat 50 cc. of the filtrate with 10 cc. of dilute sulphuric acid; no precipitation should occur.

Metals.—25 cc. of the filtrate from the above should give no colour with a few drops of sodium sulphide solution after making alkaline with ammonia.

Sulphur.—A piece of lead acetate paper held over the flask during the above digestion should not be blackened. (Beware of lead from the lead acetate paper.)

Barium Sulphide, BaS=169·4. (Ba, 81·07; S, 18·93.)—A greyish-white powder, soluble in water with decomposition into barium hydroxide and hydrosulphide.

Determination of Barium.—On 0·3 gm., as under Barium Chloride. $BaSO_4 \times 0{\cdot}726 = BaS$.

Sulphide.—Weigh out 0·4 gm. and add 50 cc. of *N*/10 iodine. Add 5 cc. of dilute hydrochloric acid and titrate back with *N*/10 thiosulphate. 1 cc. *N*/10 I ≡ 0·00847 BaS. The B.P.C. requires not less than 60 per cent. BaS. "Yellow" barium sulphide is a polysulphide and free sulphur is formed on the addition of hydrochloric acid.

Bismuth Ammonium Citrate.—This substance consists of bismuth citrate, to which ammonium citrate has been added to make it soluble. It occurs

[1] See also Cocking, *Quart. J. Pharm.*, 1928, **1**, 363.

as shining, semi-opaque scales, or as a white, odourless powder. Very soluble in water, forming a slightly alkaline solution; slightly soluble in alcohol.

Determination.—On 0·5 gm., as under Bismuth Citrate. The U.S.P. requires 46 to 52 per cent. of Bi_2O_3.

Impurities.—These may, if necessary, be tested for as under Bismuth Carbonate.

Nitrates.—As under Bismuth Carbonate.

Arsenic.—On 5 gm., as under Bismuth Salicylate. Limit, 2 parts per million.

Bismuth Carbonate, $(Bi_2O_2CO_3)_2.H_2O$=1038. (Bi, 80·54; CO_3, 11·56; H_2O, 1·74.)—Occurs in two forms known as "heavy" and "light" respectively. 5 gm. of the former, placed into a dry 25 cc. cylinder and lightly shaken down, should occupy 8 to 10 cc.; 5 gm. of the latter, under similar conditions, should occupy 15 to 25 cc. Insoluble in water and alcohol.

Determination.—Dissolve 0·2 gm. in sufficient nitric acid to keep the bismuth in solution in a bulk of about 50 cc. Add ammonia drop by drop until a slight permanent precipitate is formed. Add 2 cc. of strong nitric acid, boil, and precipitate whilst boiling by the gradual addition, slow at first, of 30 cc. of 10 per cent. diammonium phosphate solution. Dilute to 300 to 400 cc. with boiling water, allow to settle, and filter through a Gooch crucible. Wash with hot water, dry, and ignite gently. $Bi=BiPO_4\times0{\cdot}6865$; $Bi_2O_3=BiPO_4\times0{\cdot}7654$. The bismuth oxide may be also determined directly by careful ignition after adding a few drops of nitric acid, when not less than 89 per cent. of Bi_2O_3 should be left. Theory:—89·75 per cent. The B.P. requires 89 to 91 per cent.

Common Impurities.—Dissolve 2 gm. in a little nitric acid—a clear solution should result. Pour the resulting solution into about 150 cc. of water, filter, evaporate the filtrate to about one quarter of its bulk, and again filter. The filtrate should be used in the following tests.

Lead.—Add a few drops of sulphuric acid to 10 cc. of the filtrate; no cloudiness should be produced.

Copper.—Make 5 cc. of the filtrate alkaline with ammonia and allow the precipitate to settle; no blue coloration should be apparent.

Silver, Chlorides, Sulphates.—Take 3 portions of 5 cc. of the filtrate and add hydrochloric acid, silver nitrate, and barium nitrate respectively. No cloudiness should be apparent in any case.

Calcium.—Owing to the use of tap water in the precipitation of bismuth carbonate, calcium is a likely impurity. It should not amount to more than 0·25 per cent., calculated as $CaCO_3$.[1] It may be determined by dissolving 10 gm. of the sample in 30 cc. of 10 per cent. hydrochloric acid and 10 cc. of the concentrated acid. After warming to effect solution, 100 cc. of cold distilled water are added, and 15 cc. of 10 per cent. ammonia solution are run in drop by drop with constant stirring. The bismuth subchloride precipitated is filtered off, and the filtrate saturated with hydrogen sulphide. After filtering off the bismuth sulphide, the filtrate is boiled down to 20 cc., made alkaline with ammonia, and the calcium precipitated as oxalate in the ordinary manner.

Selenium and *Tellurium.*—Dissolve 1 gm. of the salt in nitric acid, add ammonium chloride, and dilute to at least 100 cc. Filter, add 10 gm.

[1] Howard and Chick, *Pharm. J.*, 1925, 115, 661.

of sodium sulphite, and allow to stand for twelve hours. No coloration should be produced.

Nitrates.—The B.P. has the following test: "On mixing 0·2 gm. with 5 drops of phenol disulphonic acid, and adding after five minutes 10 cc. of solution of ammonia (S.G. 0·959), filtering, washing the precipitate with water, and adding water to the filtrate until it measures 100 cc., the colour of the filtrate is not deeper than that obtained by similarly treating 0·0015 gm. of potassium nitrate (limit of nitrate)." This method is not by any means exact; the following[1] is much better. Mix 5 gm. of the substance with 150 cc. of water, 5 cc. of alcohol, 50 cc. of 33 per cent. sodium hydroxide solution, and 8 gm. of Devarda's alloy[2] in a round-bottomed litre flask, and allow to stand for 10 minutes. Steam distil the mixture into 10 cc. of *N*/10 hydrochloric acid, and titrate back with *N*/20 NaOH to methyl red. When 5 gm. of the salt are used, each cc. of *N*/20 acid neutralised by the ammonia produced by the reduction corresponds to 0·304 per cent. of bismuth subnitrate, $BiONO_3.H_2O$, in the salt. A blank should be carried out omitting the Devarda's alloy. This method may be used for the various salts of bismuth, except those containing ammonia.

Alkaline Carbonates.—Boil 5 gm. of the salt with 100 cc. of water for some minutes, filter, wash with boiling water, and titrate the mixed filtrates with *N*/10 sulphuric acid to methyl orange. Not more than 1 cc. should be required (B.P.).[3]

Arsenic.—Dissolve ·5 gm. in a mixture of 5 cc. of water and 20 cc. of brominated hydrochloric acid. Add stannous chloride solution drop by drop until colourless, distil 18 cc., add 40 cc. of warm water to the distillate, and proceed as usual. Limit, 2 parts per million.

Bismuth Citrate, $BiC_3H_4OH(O.CO)_3$=398·0. (Bi, 52·51; $C_3H_4OH(O.CO)_3$, 47·49.)—Insoluble in water, soluble in solution of ammonium citrate (*vide* Bismuth Ammonium Citrate, p. 51).

Determination.—On 0·5 gm., as under Bismuth Carbonate. $Bi_2O_3 \times 1{\cdot}708 = BiC_3H_4OH(COO)_3$. The U.S.P. requires 56 to 58 per cent. of Bi_2O_3.

Nitrates.—As under Bismuth Carbonate.

Arsenic.—As under Bismuth Salicylate. Limit, 2 parts per million.

Bismuth Emetine Iodide.—A double iodide of bismuth and emetine, containing 15 to 20 per cent. of bismuth and 17 to 23 per cent. of emetine. It is a brick-red powder, stable at 100° C., but decomposing above that temperature. It is dissociated by water, insoluble in alcohol, but soluble in acetone; soluble in hydrochloric acid.

Determination of Emetine.—Weigh out 0·5 gm., add 10 cc. of water and 3 cc. of ammonia, shake and allow to stand ten minutes. Add 50 cc. of ether; shake occasionally during two hours. Pipette 25 cc. of the ethereal layer through a pledget of wool into a beaker; wash the wool with ether. Evaporate off the ether gently, and dry over sulphuric acid. Dissolve the alkaloid in 20 cc. of *N*/20 sulphuric acid, and titrate back with *N*/20 sodium hydroxide to methyl red. 1 cc. *N*/20 HCl ≡ 0·01241 gm. emetine.

Bismuth.—Warm the residual liquid after the separation of the ether in order to boil off the last traces of the latter. Add 30 cc. of hydrochloric

[1] McLachlan, *Y.B.P.*, 1921, 356.

[2] Aluminium 45, copper 50, zinc 5. It may be purchased through the usual trade houses.

[3] *Cf.* Pratt, *Y.B.P.*, 1912, 506.

acid and boil. Dilute to 300 cc., boil, and filter. Add ammonia until a slight turbidity appears; then add hydrochloric acid drop by drop until the solution just becomes clear. Boil, add 50 cc. of 10 per cent. ammonium phosphate solution, and boil for several minutes. Allow to stand for half an hour. Filter through a Gooch crucible, dry, and ignite to constant weight. $BiPO_4 \times 0{\cdot}6863 = Bi$.

Bismuth Oxide, $Bi_2O_3 = 466{\cdot}0$. (Bi, 89·70; O, 10·30.)—A lemon-yellow powder, insoluble in water, but completely soluble in dilute hydrochloric acid without effervescence.

Determination.—On 0·2 gm. by precipitation as sulphide. $Bi_2S_3 \times 0{\cdot}906 = Bi_2O_3$. The oxide should not suffer appreciable loss on heating to redness.

Impurities.—The oxide should be free from the impurities mentioned under Bismuth Carbonate, which may be tested for as there given; it should also be free from carbonate.

Bismuth Phenate.—A compound of uncertain composition prepared by mixing a solution of bismuth nitrate with an alkaline solution of phenol, and washing and drying the precipitate formed. A white or greyish-white powder insoluble in water or alcohol.

Determination of Bismuth.—On 0·5 gm. by ignition as given under Bismuth Carbonate. Bi_2O_3, 80 to 84 per cent.

Phenol.—Mix 0·7 gm. with 50 cc. of water and 5 cc. of hydrochloric acid, and steam distil until no more phenol comes over. Determine the phenol in the distillate as given under Phenol. p. 163. Not less than 10 per cent. should be present.

Nitrate.—As given under Bismuth Carbonate.

Other Impurities.—See Bismuth Carbonate.

Bismuth Salicylate, $C_6H_4.OH.COO.BiO = 362{\cdot}0$. (Bi, 57·75; $C_6H_4.OH.COOH$, 38·12.)—A white, odourless powder. Insoluble in water and alcohol, but partially dissociated thereby.

Determination of Salicylic Acid.—Dissolve 0·5 gm. in dilute sulphuric acid, extract three times with ether, allow to evaporate spontaneously, and finally dry in the desiccator.[1] Titrate with $N/10$ sodium hydroxide to phenol red after weighing. 1 cc. $N/10$ NaOH $\equiv$ 0·0138 gm. $C_6H_4.OH.COOH$.

Bismuth.—On 0·5 gm. by ignition, or by precipitation as phosphate; see Bismuth Carbonate. From 62 to 65 per cent. of Bi_2O_3 should be obtained; theory, 64·36 per cent.

Free Salicylic Acid.—The B.P. requires that "when 5 gm. are shaken with 50 cc. of ether, the ethereal solution, when filtered off and evaporated (with precautions), shall leave not more than 0·005 gm. of residue (limit of free salicylic acid)," but it will usually be sufficient to shake about 1 gm. with chloroform, and add the chloroform solution to an equal volume of very dilute ferric chloride solution, when only a very faint violet coloration should be produced.

Impurities.—As under Bismuth Carbonate.

Arsenic.—Mix 5 gm. of the salt into a paste with 1 gm. of calcium hydroxide and 5 cc. of water. Dry, ignite gently, and dissolve the residue in 20 cc. of brominated hydrochloric acid and 10 cc. of water. Remove

[1] No appreciable loss of salicylic acid occurs if the ether is distilled off and the residue dried at 60° C.; *cf.* Ammonium Benzoate.

excess of bromine by adding stannous chloride solution drop by drop; distil 20 cc. and determine arsenic in the distillate as usual after adding 3 drops of stannous chloride. Limit, 2 parts per million.

Bismuth Subchloride (Bismuth Oxychloride), $BiOCl=260{\cdot}5$. (Bi, 80·23; O, 6·14; Cl, 13·63.) A white, amorphous powder. 5 gm. placed in a measuring cylinder and gently shaken down should occupy not less than 6·5 cc. Insoluble in water and alcohol; soluble in acids.

Determination.—On 0·2 gm., as under Bismuth Carbonate, by precipitating as phosphate. $BiPO_4 \times 0{\cdot}8569 = BiOCl$.

Impurities.—As under Bismuth Carbonate.

Nitrate and *Arsenic.*—As under Bismuth Carbonate.

Bismuth Subgallate, $C_6H_2.(OH)_3.COO.Bi(OH)_2=412{\cdot}1$. (Bi, 50·72; $C_6H_2.(OH)_3.COO$, 41·01.)—A citron-yellow powder. Insoluble in water, alcohol, or ether; completely soluble in sodium hydroxide solution, giving a yellow solution which rapidly changes to deep red.

Determination.—On 0·5 gm. by ignition, as under Bismuth Carbonate, $Bi_2O_3 \times 1{\cdot}769 = C_6H_2(OH)_3.COOBi(OH)_2$. Or, by precipitation as phosphate, $BiPO_4 \times 1{\cdot}3556 = C_6H_2(OH)_3.COOBi(OH)_2$. Bi_2O_3 should assay from 52 to 57 per cent.

Free Gallic Acid.—Treat 1 gm. with 20 cc. of warm alcohol, filter and wash with a little more alcohol. Evaporate the alcoholic solution to dryness, and weigh the residue. This should not exceed 0·5 per cent. (free gallic acid).

Nitrates.—As under Bismuth Carbonate.

Arsenic.—As under Bismuth Salicylate. Limit, 2 parts per million.

Bismuth Subnitrate, $Bi(OH)_2NO_3=305{\cdot}0$. (Bi, 68·52; NO_3, 20·32; H_2O, 5·90.)—Insoluble in water and alcohol; soluble in acids.

Determination.—On 0·5 gm. by ignition, as given under Bismuth Carbonate. $Bi_2O_3 \times 1{\cdot}310$ or $BiPO_4 \times 1{\cdot}003 = Bi(OH)_2NO_3$. The residue on ignition is usually 79 to 82 per cent. The theoretical percentage for one molecule of water is 76·4 per cent., but the commercial salt rarely contains this.[1]

Impurities.—It should be free from the impurities given under Bismuth Carbonate, which may be tested for as there given; it should also be free from carbonate.

Calcium Phosphate.—Dissolve 1 gm. of the salt in nitric acid, add 2 gm. of citric acid, and make alkaline with ammonia; no precipitate should be formed.

Arsenic.—Heat 5 gm. in a porcelain dish with 2 cc. of conc. sulphuric acid until white fumes are evolved. Continue as under Bismuth Carbonate. Limit, 2 parts per million.

Bismuth Sodium Tartrate.—A compound of uncertain composition,[2] consisting of varying amounts of bismuth in combination with sodium tartrate or potassium sodium tartrate. The bismuth sodium tartrates on the market may be divided into two classes: (1) "Neutral" preparations for injection in aqueous solution, or suspended in oil; (2) "acid" preparations for oral administration. The bismuth content is very variable, varying from 30 to 60 per cent.

Determination of Bismuth.—As under Bismuth Carbonate by precipitation as phosphate.

[1] Cf. *Analyst*, 1910, 35, 118.

[2] Corfield and Adams, *Y.B.P.*, 1923, 576.

Tartaric Acid.—Dissolve 0·5 gm. in a small quantity of hydrochloric acid, and dilute as far as possible without causing precipitation. Saturate with hydrogen sulphide, filter off the bismuth sulphide, and wash with water until free from chloride. Evaporate the filtrate and washings to dryness. Dissolve the residue in about 10 cc. of cold water, add an excess of potassium carbonate, followed by glacial acetic acid in sufficient quantity to neutralise the excess of potassium carbonate, and an additional 5 cc. of the acid. Add 50 cc. of 95 per cent. alcohol, and stir vigorously. After standing overnight, filter, and wash the precipitate with alcohol. Dissolve it in boiling water, and titrate with $N/10$ NaOH to phenol red to a red colour. 1 cc. $N/10$ NaOH $\equiv$ 0·01501 gm. tartaric acid.

Impurities.—See Bismuth Carbonate.

Bismuth Tribromophenate (Xeroform).—A compound of variable composition, consisting of bismuth oxide combined with tribromophenol. It is an amorphous, yellow, nearly odourless powder. Nearly insoluble in water and alcohol; decomposed by alkalies and strong acids.

Determination of Bismuth.—Ignite 0·5 gm. carefully, moisten with dilute nitric acid, evaporate down, and ignite to Bi_2O_3. From 45 to 55 per cent. should be present. Bismuth may be also determined by the phosphate method after boiling with sodium hydroxide, making acid with nitric acid, filtering off, and washing the precipitated tribromophenol. The latter should, after drying, melt at 90° to 95° C.

Impurities.—See Bismuth Carbonate.

Borax (Sodium Tetraborate).—$Na_2B_4O_7.10H_2O$=381·8. (Na, 12·04; H_3BO_3, 64·85; H_2O, 47·17.) It loses the whole of its water of crystallisation on ignition. Solubility in water, 3·5; in boiling water, 160; in glycerin, 60; insoluble in alcohol.

Determination.—Dissolve 2·5 gm. in 150 cc. of water, and titrate with $N/2$ hydrochloric acid to methyl red. 1 cc. $N/2$ HCl $\equiv$ 0·0505 gm. $Na_2B_4O_7$, or 0·0955 gm. $Na_2B_4O_7.10H_2O$. Add about one-third the volume of glycerin[1] and then 50 cc. of $N/2$ sodium hydroxide from a pipette, and continue the titration with sodium hydroxide to phenolphthalein or thymol blue. The total amount of sodium hydroxide used in the second titration should be twice that of the hydrochloric acid used in the first.

Common Impurities.—Copper, iron, calcium, magnesium, carbonate, sulphate, and chloride.

Arsenic.—By the general method on 2 gm. with the addition of 4 gm. of citric acid to keep the boric acid in solution. Limit, 5 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control; solution being effected by adding 3 cc. of ammonia. Limit, 5 parts per million.

Boric Acid, H_3BO_3=61·92. (B_2O_3, 56·20; H_2O, 43·80.)—On heating to redness B_2O_3 is formed, which slowly volatilises.[2] Solubility in water, 4·5; in alcohol, 10; in glycerin, 18.

Determination.—Dissolve 0·8 gm. in an aqueous solution containing at least 30 per cent. of glycerin,[1] and titrate with $N/2$ sodium hydroxide to phenolphthalein, or, more accurately, to thymol blue to a green colour. 1 cc. $N/2$ NaOH $\equiv$ 0·03096 gm. H_3BO_3.

[1] Subtract any blank due to the acidity of the glycerin.
[2] *Analyst*, 1918, 43, 138.

Common Impurities.—Copper, iron, calcium, magnesium, sulphate, and chloride.

Arsenic.—By the general method on 2 gm., solution being effected by the addition of 4 gm. of citric acid. Limit, 5 parts per million.

Lead.—By the general method, with 3 gm. in the primary solution and 1 gm. in the control, solution being effected by the addition of 3 cc. of ammonia. Limit, 25 parts per million.

Bromine (Br=79·92).—S.G., 3·14; B.Pt., 63° C. Solubility in water, 3·7; readily soluble in alcohol, ether, chloroform, carbon bisulphide, and glycerin.

Determination.—Bromine and chlorine may be determined, in the absence of iodine (*v.i.*), as follows: Add about 3 gm. of the sample (accurately weighed in a weighing bottle) to 15 gm. of potassium iodide in a 250 cc. flask, and dilute to the mark with water when solution has taken place. Titrate 25 cc. of this resulting solution with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}01269$ gm. I. If A is the amount of bromine used and B the amount of iodine liberated, then the amount of chlorine present (if 3 gm. have been used) is given by $\frac{B-1{\cdot}588A}{1{\cdot}9912}$.

Residue.—Evaporate about 2 gm. spontaneously in the fume chamber; no residue should be obtained.

Impurities.—Add ammonia to a suspension of 3 gm. of bromine in water until all colour has disappeared. A clear liquid should be obtained, free from oily drops, showing the absence of organic bromine compounds. Evaporate the solution to dryness and test the ammonium bromide for impurities as below.

Sulphuric Acid.—Take 1 gm. of the above residue, dissolve in 50 cc. of water, and add barium chloride solution; no precipitate should be obtained.

Iodine.—Dissolve 1 gm. of the above residue in 10 cc. of water, add 1 cc. of chloroform and a few drops of ferric chloride solution. No violet colour should be obtained.

Chlorine.—Dissolve 0·1 gm. of the above residue in 10 cc. of water, and add 4 cc. of ammonium carbonate solution (ammonium carbonate, 1 gm.; dilute ammonia, 1 cc.; water, 3 cc.). Add 12 cc. of $N/10$ silver nitrate solution, heat for a short time at 50° to 60° C., filter, and cool. The filtrate should show only a slight opalescence on acidifying with nitric acid.

Cadmium Iodide, CdI_2=366·2. (Cd, 30·0; I, 70·0.)—Colourless, shining crystals, becoming yellow on exposure to air. Very soluble in water, 84·5; and in absolute alcohol, 102.

Determination of Cadmium.—0·5 gm. is precipitated by hydrogen sulphide from a solution containing 2 to 7 cc. of conc. sulphuric acid in 100 cc. The precipitate is filtered, washed, and dissolved in hydrochloric acid (1 : 3). Excess of dilute sulphuric acid is then added, and the liquid evaporated to dryness, the residue being gently ignited. This residue is weighed as $CdSO_4$. $CdSO_4 \times 1{\cdot}757 = CdI_2$.

Iodine.—Dissolve 0·6 gm. in 25 cc. of water, add 50 cc. of $N/10$ $AgNO_3$, and titrate back with $N/10$ thiocyanate to ferric alum. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·01831 gm. CdI_2.

Impurities.—Tin, lead, copper, or zinc. On the addition of a large excess of ammonia the solution should remain clear and colourless. On the addition of excess of potash to a solution of cadmium iodide, and

filtration of the precipitate, the filtrate should give no precipitate with hydrogen sulphide.

Calamine.—A brownish or pink powder, free from grittiness, consisting of zinc carbonate with some silicate. It should be free from barium sulphate, calcium carbonate, and lead carbonate.

Artificial Calamine.—This is prepared from zinc sulphate by precipitation with sodium carbonate, and colouring with iron oxide or other colouring matter. Many artificial calamines consist of calcium carbonate suitably coloured.

Calcium Acetylsalicylate, $(CH_3CO.O.C_6H_4.COO)_2Ca.2H_2O$=434·3. (Ca, 9·23; $C_9H_7O_4$, 76·9.)—Solubility in water, 15; in alcohol, 0·12.

Calcium.—Heat 1 gm. with strong sulphuric acid; finally ignite and weigh as calcium sulphate. $CaSO_4 \times 3{\cdot}191 = Ca(C_9H_7O_4)_2.2H_2O$. Theory requires 31·3 per cent. of $CaSO_4$.

Acetylsalicylic Acid.—This may be determined by extraction with chloroform from an acidified aqueous solution. The extracted acid should have the characteristics and answer to the tests given under Acetylsalicylic Acid, but allowance must be made for a certain amount of hydrolysis of the acid during extraction.

Calcium Bromide, $CaBr_2$=199·9. (Ca, 20·05; Br, 79·95.)—A hygroscopic powder. Solubility in water, 140; in alcohol, 70; insoluble in chloroform and ether.

Determination.—Weigh out about 0·4 gm. in a weighing bottle, dissolve in 25 cc. of water, add 2 cc. of dilute nitric acid and 50 cc. of *N*/10 silver nitrate, and titrate back with *N*/10 thiocyanate solution. 1 cc. *N*/10 $AgNO_3 \equiv 0{\cdot}01999$ gm. $CaBr_2$. Calcium bromide is usually more or less hydrated. The U.S.P. requires at least 84 per cent. of the anhydrous salt.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. For the electrolytic method, 2 gm. are evaporated with 2 cc. of sulphuric acid, and treated by the general method.

Calcium Carbonate (Precipitated Chalk), $CaCO_3$=100·1. (Ca, 40·04; CO_2, 43·96.)—Insoluble in water, soluble in dilute acids with effervescence.

Determination of Calcium.—Dissolve 0·4 gm. in a small quantity of hydrochloric acid and about 20 cc. of water, and boil for a few minutes. (Guard against loss by spurting.) Add methyl red and neutralise with ammonia. Add 1 cc. of 2*N* hydrochloric acid, and dilute to 200 cc. Heat to boiling, add 25 cc. of a saturated solution of ammonium oxalate, make alkaline with ammonia, boil, and allow to stand at least one hour. Filter through a Gooch crucible, wash by decantation on the filter with dilute ammonia solution, keeping the volume of the washing water as low as possible. The precipitate may be weighed as calcium oxalate by drying at 100° C., calcium carbonate by heating to 500° C., or calcium oxide by heating over a Meker burner for one hour. $CaC_2O_4.H_2O \times 0{\cdot}685 = CaCO_3$; $CaO \times 1{\cdot}785 = CaCO_3$. Alternatively, the precipitate of calcium oxalate may be dissolved in a small quantity of warm dilute hydrochloric acid, diluted with water, sulphuric acid added, and the oxalic acid titrated with *N*/10 permanganate. 1 cc. *N*/10 $KMnO_4 \equiv 0{\cdot}005004$ gm. $CaCO_3$.

Carbonate.—On 0·25 gm., as given under Sodium Carbonate. $CO_2 \times 2{\cdot}274 = CaCO_3$.

Common Impurities.—Iron, aluminium, magnesium, phosphate, chloride, and sulphate.

Solubility.—1 gm. treated with 50 cc. of water should yield a filtrate neutral to litmus, and which on evaporation leaves no residue.

Arsenic.—On 2 gm., as under Ammonium Carbonate. Limit, 5 parts per million.

Lead.—By the acid method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Calcium Chloride, $CaCl_2$=111·0. (Ca, 36·10; Cl, 63·90.)—Calcium chloride occurs as very deliquescent crystals ($CaCl_2 . 6H_2O$=219·1). The anhydrous salt is obtained by carefully drying these at a temperature not exceeding 200° C.; at higher temperatures decomposition may result, with production of a basic alkaline salt, and even at 200° C. a small amount of this compound is formed. The B.P. requires that calcium chloride shall not lose more than 5 per cent. when dried at 200° C. Solubility in water, 70; in alcohol, 30.

Determination of Calcium.—On 0·3 gm., as given under Calcium Carbonate. $CaO \times 1{\cdot}980 = CaCl_2 . CaO \times 3{\cdot}907 = CaCl_2 . 6H_2O$.

Chloride.—On 0·2 gm., as given under Barium Chloride. 1 cc. $N/10$ $AgNO_3 \equiv 0{\cdot}00555$ gm. $CaCl_2$, or 0·01095 gm. $CaCl_2.6H_2O$.

Hypochlorite.—The salt should not evolve chlorine when treated with hydrochloric acid.

Barium.—An aqueous solution should give no precipitate with a saturated aqueous solution of calcium sulphate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. For the electrolytic process use the method for Chlorides, Bromides, and Iodides (p. 33).

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 20 parts per million.

Calcium Formate, $Ca(HCOO)_2$=130·1. (Ca, 30·80; H.COO, 69·20.)—Solubility in water, 16·5; insoluble in alcohol.

Determination of Calcium.—If necessary, on 0·3 gm., as given under Calcium Carbonate.

Formate.—Dissolve 0·8 gm. in water and dilute to 100 cc. Remove 10 cc. of this solution and place in a flask with a slight excess of sodium carbonate and 50 cc. of $N/10$ potassium permanganate, and warm for fifteen minutes on the water bath. Add 25 cc. of $N/10$ oxalic acid and excess of sulphuric acid, and titrate with $N/10$ potassium permanganate. The total volume of $N/10$ permanganate used, less 25 cc., gives the amount absorbed by the formate. 1 cc. $N/10$ $KMnO_4 \equiv 0{\cdot}00325$ gm. $Ca(HCOO)_2$.

Arsenic.—Weigh 2 gm. and char thoroughly in a porcelain dish. Treat the residue with 14 cc. of brominated hydrochloric acid and 50 cc. of warm water. Remove the excess of bromine with stannous chloride solution, and proceed as usual. Limit, 5 parts per million. The electrolytic method may be carried out directly on the salt.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Calcium Glycerophosphate, $CaPO_4(OH)_2 . C_3H_5$=210·2. (Ca, 19·07; P, 14·77.)—A white, amorphous powder, free from odour. The amount of water present may vary from 10 to 20 per cent. Commercial calcium glycerophosphate consists of a mixture of the α and β salts. In some

cases an addition of citric or other organic acid is made to increase the solubility.

Solubility.—Owing to the different solubilities of the α and β salts (1·6 and 5·0 respectively), the commercial salt varies in solubility, but when 1 gm. is mixed with 40 cc. of water, 90 per cent. should dissolve, and on the addition of a further 100 cc. of water the whole should go into solution. Calcium glycerophosphate is practically insoluble in boiling water and in alcohol.

Determination of Calcium.—The glycerophosphate should contain at least 15 per cent. of calcium. 1·0 gm. should be precipitated as oxalate; see Calcium Carbonate. $CaO \times 3{\cdot}75 = CaPO_4(OH)_2C_3H_5$.

Total Phosphate.—Ignite 0·5 gm., dissolve the residue in dilute nitric acid, and proceed with the estimation of phosphate as under Magnesium Glycerophosphate. $Mg_2P_2O_7 \times 1{\cdot}887 = CaPO_4(OH)_2.C_3H_5$; $Mg_2P_2O_7 \times 0{\cdot}8534 = PO_4$.

Free Phosphoric Acid.—To 0·1 gm. dissolved in 5 cc. of 25 per cent. nitric acid add 5 cc. of ammonium molybdate solution and warm. No immediate precipitate should be formed.[1]

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—Weigh out 2 gm. and add 25 cc. of 5 per cent. sulphuric acid. Filter, and wash the residue five or six times with 25 cc. of 5 per cent. sulphuric acid to which 5 cc. of alcohol have been added. Digest the residue with 50 cc. of hot ammoniacal ammonium acetate solution, pouring through the filter two or three times. Wash the filter paper, evaporate to 40 cc. if necessary, and determine the lead by adding potassium cyanide and sodium sulphide in the usual manner. The standard should contain 25 cc. of ammoniacal ammonium acetate solution.

Calcium Hydroxide, $Ca(OH)_2 = 74{\cdot}1$. (Ca, 54·08; H_2O, 24·32; CaO, 75·68.)—Solubility in water, 0·17; in boiling water, 0·08; more soluble in solution of sucrose.

Determination of Calcium. — On 0·2 gm., as given under Calcium Carbonate. $CaO \times 1{\cdot}321 = Ca(OH)_2$.

Hydroxide.—On 0·4 gm. in 25 cc. of $N/2$ hydrochloric acid; boil for a few minutes, and titrate back with $N/2$ sodium hydroxide to methyl thymol blue. 1 cc. $N/2$ HCl $\equiv$ 0·01852 gm. $Ca(OH)_2$.

Impurities.—As under Calcium Oxide.

Calcium Hypophosphite, $Ca(H_2PO_2)_2 = 170{\cdot}2$. (Ca, 23·55; P, 36·48.)—Solubility in water, 12·5; insoluble in alcohol. When heated, spontaneously inflammable vapours are given off, whilst an aqueous solution reduces potassium permanganate.

Determination.—Dissolve 5 gm. in 80 cc. of water, add 10 cc. of lead acetate solution (10 gm. of lead acetate in 100 cc. of recently boiled, distilled water), and make up to 100 cc. Shake, and allow to stand one hour. Pipette off 10 cc. of the clear liquid, and add 50 cc. of potassium dichromate, and 10 cc. of conc. sulphuric acid. Heat on the water bath for one hour, cool, and make up to 250 cc. with water. To 25 cc. of this solution add 2 gm. of potassium iodide, and titrate with $N/10$ sodium thiosulphate, using starch indicator, the change of colour being from blue to pale green. 1 cc. N $K_2Cr_2O_7 \equiv 0{\cdot}02127$ gm. $Ca(H_2PO_2)_2$. It is advisable to carry out a blank experiment omitting the hypophosphite.[2]

[1] See Lizius, *Y.B.P.*, 1921, 360. [2] Cocking and Kettle, *Y.B.P.*, 1913, 518.

Common Impurities.—Copper, iron, magnesium, sulphate, chloride, and phosphate. The solution in water should be clear.

Arsenic.—On 1 gm. by the methods given on pp. 33 and 51. Limit, 5 parts per million.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Calcium Iodide, CaI_2=293·9. (Ca, 13·63; I, 86·37.)—A white, deliquescent mass, becoming yellow on keeping. Solubility in water, 200; very soluble in alcohol.

Determination of Calcium.—On 0·4 gm., as given under Calcium Carbonate. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·01469 gm. CaI_2.

Iodide.—On 1 gm., as given under Ammonium Bromide. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·01469 gm. CaI_2. From 80 to 85 per cent. of anhydrous calcium iodide should be present.

Arsenic.—By the general method on 2 gm. Limit, 10 parts per million.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Calcium Lactate, $Ca(C_3H_5O_3)_2.5H_2O$=308·3. (Ca, 13·00; $C_3H_5O_3$, 57·77; H_2O, 29·23.)—A white and practically odourless powder. Solubility in water, 5·4; slightly soluble in alcohol, insoluble in ether.

Determination of Calcium.—Heat 1 gm. in a porcelain crucible with strong sulphuric acid; repeat the process until the residue is quite white. Ignite until the weight is constant. $CaSO_4 \times 0{\cdot}2944 = Ca$; $CaSO_4 \times 2{\cdot}264 = Ca(C_3H_5O_3)_2.5H_2O$; $CaSO_4 \times 1{\cdot}602 = Ca(C_3H_5O_3)_2$.

The B.P. requires that from 0·410 to 0·450 gm. of residue shall be obtained from 2 gm. of the lactate, which is equivalent to 92·7 to 104·2 per cent. of the hydrated lactate.

Water.—The U.S.P. states that the salt loses from 25 to 29·2 per cent. at 120° C.

Acidity.—The salt should not be alkaline. 1 gm. dissolved in 50 cc. of water should not give a blue colour with thymolphthalein solution.

Arsenic.—By the general method on 2 gm., using 12 cc. of acid. Limit, 5 parts per million.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Calcium Oxide, CaO=56·1. (Ca, 71·46; O, 28·54.)—Solubility in water, 0·13; less soluble in boiling water, 0·06.

Determination of Calcium.—On 0·1 gm. by the method given under Calcium Carbonate. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·002804 gm. CaO.

Alkalinity.—Boil 0·2 gm. with 25 cc. of $N/2$ HCl, cool, and titrate back to methyl-thymol blue. 1 cc. $N/2$ NaOH $\equiv$ 0·01402 gm. CaO.

Common Impurities.—Iron, aluminium, magnesium, chloride, phosphate, sulphate, and carbonate. The substance should dissolve completely in hydrochloric acid with only slight effervescence to a clear solution.

Arsenic.—By the method given under Barium Carbonate on 2 gm. Limit, 5 parts per million.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Calcium Phosphate, $Ca_3(PO_4)_2$=310·3. (Ca, 38·74; PO_4, 61·26.)—Ordinary precipitated calcium phosphate usually consists of a mixture of $CaHPO_4$ and $Ca_3(PO_4)_2$. Insoluble in water, soluble in dilute acids.

Determination of Calcium.—Weigh 0·12 gm., dissolve in a small quantity of dilute hydrochloric acid; add 5 gm. of sodium acetate and some acetic acid, heat to boiling, and add a solution containing 2 gm. of ammonium oxalate. Complete the process as given under Calcium Carbonate. 1 cc. $N/10$ $KMnO_4 \equiv 0{\cdot}005172$ gm. $Ca_3(PO_4)_2$.

Common Impurities.—Copper, iron, magnesium, carbonate, chloride, sulphate, and silica.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—Weigh out 2 gm., and add 25 cc. of 5 per cent. sulphuric acid. Filter, and wash the residue five or six times with 25 cc. of 5 per cent. sulphuric acid to which 5 cc. of alcohol have been added. Digest the residue with 50 cc. of hot ammoniacal ammonium acetate solution, pouring through the filter two or three times. Wash the filter paper, evaporate to 40 cc. if necessary, and determine the lead by adding potassium cyanide and sodium sulphide in the usual manner. The standard should contain 25 cc. of ammoniacal ammonium acetate solution.

Calcium Sulphate, $CaSO_4.2H_2O=172{\cdot}2$. (Ca, 23·27; SO_4, 55·80; H_2O, 20·93.)—Solubility in water, 0·26; rather more soluble in dilute hydrochloric acid.

Determination of Calcium.—On 0·2 gm., as given under Calcium Carbonate. 1 cc. $N/10$ $KMnO_4 \equiv 0{\cdot}008608$ gm. $CaSO_4.2H_2O$, or 0·006807 gm. $CaSO_4$.

Sulphate.—On 0·2 gm., as under Sodium Sulphate. $BaSO_4 \times 0{\cdot}583 = CaSO_4$; $BaSO_4 \times 0{\cdot}737 = CaSO_4.2H_2O$.

Common Impurities.—Iron, magnesium, carbonate.

Plaster of Paris.—On heating to 120° C. the so-called "anhydrous" calcium sulphate is formed, $2CaSO_4.H_2O$, or Plaster of Paris. It should be free from the above impurities, and when mixed with half its weight of water should form a smooth paste, setting to a hard mass in about five minutes. If the heating is carried out at much above 200° C. the power of setting may be seriously impaired.

Calcium Sulphide (*Calx Sulphurata*).—A substance prepared by heating a mixture of calcium sulphate and carbon, and consisting principally of a mixture of calcium sulphide and calcium sulphate.

Determination.—The B.P. requires that it shall not contain less than 50 per cent. of CaS, the determination being carried out as follows: Place 0·8 gm. in a stoppered flask with 50 cc. of water in which 1·4 gm. of copper sulphate have been dissolved. Add a little hydrochloric acid, heat nearly to boiling, shake for ten minutes, and filter. The filtrate should give no reaction for copper with potassium ferrocyanide, showing that a due proportion of calcium sulphide is present.

Calx Chlorinata (Bleaching Powder).—Bleaching powder is produced by the action of chlorine gas upon moist slaked lime, and has approximately the formula Ca.OCl.Cl. This formula indicates about 43 per cent. of available chlorine, but commercial samples do not often contain more than 37 per cent.

Determination.—The amount of available chlorine (on which the commercial value of the sample depends) may be determined as follows: Treat 0·3 gm. with water, making sure that all lumps are broken down; add 10 cc. of a 10 per cent. potassium iodide solution and slight excess of hydrochloric acid. Titrate the liberated iodine with $N/10$ thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}003546$ gm. available chlorine. It should contain not less than 30 per cent. of available chlorine.

Cerium Oxalate, $Ce_2(C_2O_4)_3.10H_2O$=724·7.—Cerium oxalate, as used for medicinal purposes, consists of cerium oxalate mixed with the oxalates of other rare elements. It occurs as a slightly pink powder, insoluble in water. It dissolves in dilute hydrochloric acid without effervescence.

Determination.—On ignition it leaves not less than 47 per cent. of a reddish-brown residue.

Charcoal. *Wood Charcoal.*—The ash should not be more than 7·5 per cent. If 1 gm. is boiled for a few minutes with 5 cc. of sodium hydroxide solution and 15 cc. of water, and filtered, the colour of the filtrate should not be deeper than pale yellow (B.P.).

Animal Charcoal.—The purified variety should not yield more than 10 per cent. of ash, and should pass the above test with sodium hydroxide.

Chromic Anhydride, CrO_3=100·0. (Cr, 52·00; O, 48·00.)—Red, deliquescent crystals, M.Pt., 192° C. Solubility in water, 170; decomposes alcohol.

Determination.—Dissolve 0·1 gm. in water, add 2 gm. of potassium iodide, and a slight excess of hydrochloric acid, and titrate the liberated iodine with *N*/10 thiosulphate. 1 cc. *N*/10 $Na_2S_2O_3 \equiv$ 0·003334 gm. CrO_3.

Loss on Ignition.—On heating to redness, Cr_2O_3 remains. The calculated residue is 70·0 per cent.

Sulphate.—If it is to be used as a reagent the anhydride may be tested by heating half a gram to redness in a porcelain crucible, extracting the residue with water, and filtering. The filtrate should not leave more than five milligrams of residue on evaporation to dryness. The commercial substance should be treated as follows: Dissolve 4 gm. in a mixture of 20 cc. of water and 10 cc. of conc. hydrochloric acid. Add 5 cc. of 10 per cent. barium chloride solution, and filter. Add more barium chloride solution to the filtrate, when no precipitation should take place, giving a limit of 8·2 per cent. for sodium sulphate.

Cobalt Nitrate, $Co(NO_3)_2.6H_2O$=291·1; $Co(NO_3)_2$=183·0. (Co, 20·26; NO_3, 22·60; H_2O, 37·14.)—Solubility in water, 100; in alcohol, 200.

Determination.—Weigh out 1 gm., dissolve in 250 cc. of water, and precipitate by adding a slight excess of sodium hydroxide. The precipitate is filtered, washed with hot water, and dried. It is reduced to metallic cobalt in an atmosphere of hydrogen, washed with water to remove traces of alkali, and weighed. Co×3·103=$Co(NO_3)_2$; Co×4·936=$Co(NO_3)_2.6H_2O$.

Alkalis.—Dissolve 2 gm. in water, precipitate by adding excess of ammonia and ammonium sulphide, filter, evaporate the filtrate to dryness, and ignite. Not more than 5 mg. of residue should be obtained.

Heavy Metals.—2 gm. dissolved in water, and slightly acidified with hydrochloric acid, should not show any darkening on the addition of sulphuretted hydrogen.

Zinc.—Dissolve 1 gm. in water, and boil with excess of sodium hydroxide. On filtering and adding ammonium sulphide to the filtrate no cloudiness should be observed.

Nickel.—Dissolve 1 gm. in 20 cc. of water, add 1·5 gm. of potassium cyanide, and warm until the solution becomes yellow. Filter, cool, add 1 cc. of bromine to the filtrate, and shake until dissolved. Add 10 cc. of 15 per cent. sodium hydroxide solution. A black precipitate indicates nickel.

Copper Acetate, $Cu(C_2H_3O_2)_2.H_2O$ = 199·6. (Cu, 31·85.)—This salt

crystallises in bluish-green crystals. Solubility in water, 7·7; in alcohol, 7·1. On ignition it yields 39·9 per cent. of cupric oxide.

Basic Copper Acetate, or *Verdigris*, is a compound of varying composition, usually containing from 43 to 50 per cent. of cupric oxide as determined by ignition. Only partially soluble in water, but almost entirely soluble in ammonia.

Copper may be determined as under Cupric Chloride.

Common Impurities.—Calcium, sulphate, and metallic copper. The last may be detected in the residue insoluble in ammonia.

Cupric Chloride, $CuCl_2.2H_2O$=170·52. (Cu, 37·28; Cl, 41·59; H_2O, 21·13.)—Green, deliquescent crystals; a dark brown solid when anhydrous. Solubility in water, 95; easily soluble in alcohol.

Determination of Copper.—Dissolve 0·5 gm. in 250 cc. of water, and heat to boiling; then add a slight excess of sodium hydroxide in small quantities at a time with constant stirring, boil gently for a few minutes, and allow to settle. Wash by decantation, filter, wash thoroughly with boiling water, and dry. Ignite the precipitate apart from the paper, and treat with a few drops of nitric acid before the final ignition. CuO×0·7989=Cu; CuO×1·690=$CuCl_2$; CuO×2·143=$CuCl_2.2H_2O$.

Chloride.—On 0·2 gm., as given under Ammonium Chloride. 1 cc. *N*/10 $AgNO_3$ ≡0·008526 gm. $CuCl_2$, $2H_2O$, or 0·007250 gm. $CuCl_2$.

Alkalis.—2 gm. tested as under Cobalt Nitrate, or as under Cupric Sulphate should give not more than 2 mg. of residue.

Lead.—2 gm. dissolved in 10 cc. of water should not show any precipitate on standing after the addition of a few drops of sulphuric acid.

Iron.—As given under Cupric Sulphate.

Sulphate.—Dissolve 1 gm. in 20 cc. of water and 1 cc. of hydrochloric acid, and add 5 cc. of barium chloride solution. There should be no turbidity within five minutes.

Cupric Sulphate, $CuSO_4.5H_2O$=249·7. (Cu, 25·46; SO_4, 38·47; H_2O, 36·07.)—Blue, transparent crystals or blue powder. Loses four molecules of water at 100° C., the fifth at 230° C. Solubility in water, 19; in glycerin, 4; insoluble in alcohol.

Determination of Copper.—On 1 gm., as given under Cupric Chloride. CuO×0·7989=Cu; CuO×3·138=$CuSO_4.5H_2O$.

Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4$× 1·0697=$CuSO_4.5H_2O$.

Iron.—Dissolve 5 gm. in 25 cc. of water, and add 2 cc. of conc. nitric acid. Boil, cool, and add excess of ammonia. Filter and wash with a 1 per cent. ammonia solution. Dissolve the precipitate in dilute hydrochloric acid, and reprecipitate with ammonia. Ignite and weigh as Fe_2O_3. B.P. limit, not more than 0·14 per cent. Fe_2O_3. For reagent purposes not more than 0·02 per cent. Fe_2O_3 should be present.

Other Impurities.—Dissolve 1 gm. in water, precipitate with sulphuretted hydrogen, filter, evaporate the filtrate to dryness, and ignite. Not more than 2 mg. of residue should be obtained.

Chloride.—No opalescence should be observable on the addition of silver nitrate to a solution of 1 gm. of the salt in 20 cc. of water, acidified with nitric acid.

Lead.—2 gm. dissolved in 10 cc. of water should not show any precipitate on standing after the addition of a few drops of sulphuric acid.

Arsenic.—Dissolve 1 gm. in 10 cc. of water and 15 cc. of stannated hydrochloric acid, and distil 20 cc. Add a slight excess of bromine solution to the distillate, remove excess of bromine by means of stannous chloride solution, and continue as usual. Limit, 10 parts per million.

Ferric and Ammonium Citrate.—The B.P. preparation consists of thin, dark red, transparent scales. Another variety, known as "green," forms greenish deliquescent scales. Solubility in water, about 200. A 2 per cent. solution should be only faintly acid ($pH=4$ to 6).

Determination of Iron.—Dissolve 1 gm. in 25 cc. of water and 7 cc. of hydrochloric acid. Add 4 gm. of potassium iodide, and keep at 40° C. in a stoppered bottle for thirty minutes. Cool, add 100 cc. of water, and titrate the liberated iodine with $N/10$ thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·005584 gm. Fe. The B.P. requires 31 to 32 per cent. Fe_2O_3, *i.e.* 21·68 to 22·38 per cent. Fe. The "green" variety contains 13 to 14 per cent. Fe; the U.S.P. requires 16 to 18 per cent. Fe.

Sulphate.—Not more than traces should be present.

Arsenic.—Mix 2 gm. into a paste with 1 gm. of calcium hydroxide and 2 cc. of water. Dry, and ignite gently. Dissolve the residue in 20 cc. of brominated hydrochloric acid and 10 cc. of water. Remove excess of bromine with stannous chloride solution, and distil 24 cc. Determine the arsenic in the distillate as usual. Limit, 5 parts per million. For the electrolytic process the general method may be used.

Ferric Ammonium Sulphate (Iron Alum), $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O=964·3$. ($NH_3$, 3·53; Fe, 11·58; SO_4, 39·84; H_2O, 44·84.)—White crystals with a faint purple tinge. Loses the whole of its water of crystallisation at 230° C. Solubility in water, 124 at 25° C. Insoluble in alcohol.

Determination of Ammonia.—On 8 gm., as given under Ammonium Sulphate. 1 cc. $N/2$ $HCl \equiv 0·008515$ gm. NH_3, or 0·2411 gm. $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, or 0·1330 gm. $(NH_4)_2SO_4.Fe_2(SO_4)_3$.

Iron.—On 1 gm. by precipitation with ammonia in the ordinary way. $Fe_2O_3 \times 0·6994 = Fe$. $Fe_2O_3 \times 6·039 = (NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$. $Fe_2O_3 \times 3·332 = (NH_4)_2SO_4, Fe_2(SO_4)_3$.

Sulphate.—On 0·4 gm., as given under Sodium Sulphate. $BaSO_4 \times 1·033 = (NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$. $BaSO_4 \times 0·5698 = (NH_4)_2SO_4.Fe_2(SO_4)_3$. $BaSO_4 \times 0·4115 = SO_4$.

Common Impurities.—Copper, calcium, iron, potassium, and chloride.

Alkalis.—Dissolve 2 gm. in water, boil with 1 cc. of nitric acid, and add excess of ammonia. Filter, evaporate the filtrate to dryness, and ignite. Not more than 2 mg. of residue should be obtained.

Ferric Chloride, $FeCl_3.6H_2O=270·3$. $FeCl_3=162·2$. (Hydrated salt—Fe, 20·66; Cl, 39·35; H_2O, 39·99.)—Forms hexagonal crystals which appear greenish by reflected light and dark red by transmitted light; usually, however, the commercial salt is an orange coloured, hygroscopic, crystalline mass with a slight odour of hydrochloric acid. Solubility in water, 140; easily soluble in alcohol, ether, and glycerin.

Determination.—Dissolve about 1 gm., weighed in a stoppered weighing bottle, in 25 cc. of water; add 3 cc. of hydrochloric acid and 4 gm. of potassium iodide, and keep in a stoppered flask at 40° C. for half an hour. Cool, dilute with 100 cc. of water, and titrate with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0·005584$ gm. Fe, 0·01622 gm. $FeCl_3$, or 0·02703 gm. $FeCl_3.6H_2O$.

Impurities.—Alkalis as under Ferric Ammonium Sulphate. Ferrous salts and nitrates should be absent.

Lead.—As under Cupric Chloride.

Arsenic.—Heat 0·5 gm. with 1 cc. of conc. sulphuric acid until white fumes are evolved. Dissolve the residue in 10 cc. of water, add 15 cc. of brominated hydrochloric acid, and then stannous chloride solution until colourless. Distil 20 cc., add a slight excess of solution of bromine to the distillate, remove excess with stannous chloride solution, and continue as usual. Limit, 20 parts per million. In the electrolytic method heat 0·5 gm. with 1 cc. of conc. sulphuric acid until white fumes are evolved. Continue as for iron salts. The anhydrous salt is used for reagent purposes. It is a black, hygroscopic powder. It should be free from sulphate, nitrate, free chlorine, and ferrous salts, and should not contain more than 50 parts of arsenic per million.

Ferric Citrate.—Forms thin, transparent, garnet-red scales, slowly but completely soluble in cold water, readily in hot water. The solubility diminishes with age of preparation.

Determination.—Dissolve 0·5 gm. in 15 cc. of water, add 2 cc. of hydrochloric acid and 1 gm. of potassium iodide, and keep at 40° C. for half an hour. Cool, and titrate the liberated iodine with $N/10$ thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}005584$ gm. Fe. Not less than 16 per cent. of iron should be present.

Ammonia.—No ammonia should be evolved on heating 1 gm. with solution of sodium hydroxide.

Arsenic.—On 2 gm., as given under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferric Formate, $Fe_3(OH)_2(HCOO)_7.4H_2O$=588·7. (Fe, 28·47; H.COO, 53·48; H_2O, 12·23.)—Commercial ferric formate is a basic salt. It occurs as fine needles or as a gritty, coppery-red powder. Solubility in water, 5·5. The solution is liable to decomposition with deposition of ferric hydroxide or basic formates.

Determination of Iron.—Ignite 1 gm. carefully until constant in weight. The calculated residue is 40·68 per cent. $Fe_2O_3 \times 2{\cdot}46 = Fe_3(OH)_2(H.COO)_7.4H_2O$.

Formate.—Dissolve 0·8 gm. in 50 cc. of water, and precipitate by adding a slight excess of sodium hydroxide. Filter, well wash the precipitate, and determine the formic acid in the mixed filtrate as under Calcium Formate. 1 cc. $N/10$ $KMnO_4 \equiv 0{\cdot}004205$ gm. $Fe_3(OH)_2(H.COO).4H_2O$.

Arsenic.—As under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferric Glycerophosphate.—Yellow scales or a yellowish powder. Slightly soluble in water.

Determination of Iron.—Dissolve 1 gm. in 200 cc. of water in a stoppered flask or bottle. Add 5 gm. of potassium iodide and 15 cc. of hydrochloric acid, and allow to stand for one hour at 40° C. Titrate the liberated iodine with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}005584$ gm. Fe. The salt should contain about 15 per cent. of iron.

Phosphate.[1]—Dissolve 1 gm. in a mixture of 15 cc. of water and 5 cc. of dilute nitric acid. Add 10 cc. of 20 per cent. sodium hydroxide solution, filter, and wash to 50 cc. This solution is then run from a burette into

[1] Lizius, *Y.B.P.*, 1921, 360.

a Nessler cylinder containing 10 cc. of 25 per cent. nitric acid and 10 cc. of 10 per cent. ammonium molybdate until the colour so produced is equal to that produced in a similar Nessler cylinder to which has been added 5 cc. of standard phosphoric acid solution. 1 cc. ≡ 0·00004 gm. H_3PO_4.

Arsenic.—On 2 gm., as given under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferric Hydroxide, $Fe(OH)_3$=108·9. (Fe, 52·25; OH, 47·75.)—A brown or reddish-brown powder, insoluble in water, but readily soluble in hydrochloric acid without effervescence.

Determination.—Dissolve 0·3 gm. in hydrochloric acid, dilute to about 200 cc., and precipitate with excess of ammonia. Filter, wash thoroughly with boiling water, and ignite to Fe_2O_3. $Fe_2O_3 \times 1{\cdot}339 = Fe(OH)_3$. The calculated percentage of Fe_2O_3 is 74·7, but commercial samples usually range from 80 to 85 per cent.

Arsenic.—Dissolve 2 gm. in 15 cc. of hydrochloric acid and 10 cc. of water, add stannous chloride solution until the yellow colour disappears, distil 20 cc., add a little bromine solution, and remove the excess of bromine by a few drops of stannous chloride solution. Add 40 cc. of warm water, and determine as usual. Limit, 5 parts per million. The electrolytic method may be carried out directly with the addition of 2 gm. of citric acid.

Ferric Hypophosphite, $Fe(H_2PO_2)_3$=251·0. (Fe, 22·25; H_2PO_2, 77·75.)—A white or greyish-white powder, slightly soluble in water. Soluble in sodium citrate solution to a pale green solution.

Qualitative Test.—Boil 1 gm. with 10 cc. of acetic acid, filter, and add a few drops of the filtrate to excess of mercuric chloride solution. A white precipitate of mercurous chloride is produced on warming.

Calcium.—The filtrate from the above qualitative test should be tested with ammonium oxalate.

Determination of Iron.—Dissolve 1 gm. in sodium citrate solution, and precipitate with excess of sodium hydroxide solution. Well wash the precipitate by decantation and redissolve in hydrochloric acid. Reprecipitate by ammonia, filter, wash, and ignite to Fe_2O_3. $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

Hypophosphite.—This may be determined by the method of Cocking and Kettle [1] (see p. 60),

Arsenic.—Mix 1 gm. with 2 gm. of potassium chlorate and 20 cc. of hydrochloric acid, and allow to stand for one hour. Warm gently to expel chlorine, and add slight excess of stannous chloride solution. Add 10 cc. of water and distil 24 cc. To the distillate add 35 cc. of hot water, 3 drops of stannous chloride solution, and continue as usual. Limit, 5 parts per million. For the electrolytic method treat 1 gm. by the general method for Hypophosphites (p. 33). Add 2 gm. of citric acid, and continue as usual.

Ferric Oxide, Fe_2O_3=159·7. (Fe, 69·94; O, 30·06.)—A red powder, insoluble in water; soluble with difficulty in boiling concentrated hydrochloric acid.

Determination.—Dissolve 0·3 gm. in boiling concentrated hydrochloric acid, dilute to about 200 cc., and add excess of ammonia. Filter, wash thoroughly with boiling water, ignite, and weigh as Fe_2O_3. $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

Arsenic.—As under Ferric Hydroxide. Limit, 5 parts per million.

[1] *Y.B.P.*, 1913, 521.

Ferric Phosphate, Soluble.—Soluble ferric phosphate, U.S.P., is ferric phosphate rendered soluble by the presence of sodium citrate. It forms green, transparent scales which become discoloured on exposure to light. Completely soluble in water, insoluble in alcohol.

Qualitative Tests.—The aqueous solution is not precipitated by ammonia, but when boiled with potassium hydroxide a red precipitate is produced without evolution of ammonia. After filtering, acidifying the filtrate with HCl, and cooling, an abundant, white, crystalline precipitate is given with magnesia mixture and excess of ammonia. This precipitate, after washing, turns yellow when treated with a few drops of silver nitrate solution.

Determination.—On 1 gm., as given under Ferric Glycerophosphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}005584$ gm. Fe. The U.S.P. requires not less than 12 per cent. of Fe.

Arsenic.—On 2 gm. as under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferric and Potassium Tartrate. *Ferrum Tartaratum.*—Transparent, red scales, soluble in water; slightly soluble in alcohol.

Determination.—Ignite 1 gm. in a porcelain dish. Dissolve the residue in hydrochloric acid, and precipitate the iron with ammonia. Filter, wash, ignite, and weigh as Fe_2O_3. The B.P. requires not less than 30 per cent. of ferric oxide.

Arsenic.—On 2 gm., as given under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferric Pyrophosphate, Soluble.—Soluble ferric pyrophosphate is ferric pyrophosphate rendered soluble by the addition of sodium citrate. It occurs as thin, green, transparent scales, becoming discoloured on exposure to light. It is freely and completely soluble in water; insoluble in alcohol.

Determination.—On 1 gm. as given under Ferric Citrate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}005584$ gm. Fe. It should contain not less than 10 per cent. of iron.

Arsenic.—On 2 gm., as given under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferric, Quinine, and Strychnine Citrates.—These are scale preparations containing ferric and ammonium citrates, and either quinine or strychnine, or both. Solubility in water, 200. They are transparent, greenish-yellow, and deliquescent.

Determination of Iron.—Ignite carefully 1 gm.; from 18 to 20 per cent. of Fe_2O_3 should be obtained, which should be only slightly alkaline to litmus.

Total Alkaloids.—Dissolve 5 gm. in 50 cc. of water, add 10 cc. of ammonia solution, and extract the alkaloids by shaking repeatedly with chloroform. Evaporate the chloroformic extract, dry the residue at 110° C., and weigh. The quinine is obtained in the anhydrous condition together with the strychnine if present. Not less than 15 per cent. of anhydrous quinine should be present. The standard for strychnine is 1 per cent.

Strychnine.[1]—Dissolve 10 gm. in 70 cc. of water in a beaker, add 5 cc. of N sulphuric acid, and almost neutralise the whole with ammonia until the precipitated quinine only just redissolves. Add 30 gm. of Rochelle salt, and almost neutralise the liquid with dilute ammonia, the solution

[1] Harvey and Back, *Analyst*, 1921, **46**, 188.

being left faintly acid to litmus paper. Stir the mixture and heat on a water bath for fifteen minutes, cool, and transfer to a 100 cc. measuring flask, rinsing the beaker with water so as to make the volume up to 100 cc. After standing two hours, filter the liquid, rejecting the first 10 cc. Extract 50 cc. of the filtrate three times with chloroform (using 30 cc., 10 cc., and 10 cc.) and ammonia, and wash the mixed chloroform solutions twice with 5 cc. of water. Extract the chloroform with 30 cc. of 10 w/v sulphuric acid, and twice more with 10 cc. of the same acid, and collect the acid liquids in a small (60 cc.) separator previously plugged with a small piece of cotton-wool. Add 5 cc. of freshly made 4 per cent. potassium ferrocyanide solution, practically fill the separator with 10 per cent. acid (to exclude air), and, after rotation, allow the whole to stand in a dark place for two hours. It is advisable to be sure that precipitation has definitely occurred before placing aside. At the end of this time force out the acid through the plug, wash the strychnine ferrocyanide twice with 3 cc. of 5 per cent. sulphuric acid, and recover the strychnine by shaking with 10 cc. of 10 per cent. ammonia and 15, 10, and 10 cc. of chloroform. Carry out the evaporation as usual, adding about 3 drops of amyl alcohol towards the end to prevent decrepitation of the strychnine crystals. When cold, wash the alkaloidal residue three times with 1 cc. of ether, and dry at 100° C. A correction of 1·7 per cent. is made for the volume of quinine tartrate.

Arsenic.—On 2 gm., as given under Ammonium Citrate. Limit, 5 parts per million.

Ferric Valerianate, $Fe(C_5H_{11}O_4)$=190·9. (Fe, 29·25; $C_5H_{11}O_4$, 70·75.)—A dark reddish-brown amorphous powder, usually having a slight odour of valeric acid. When boiled with water the salt is decomposed, ferric oxide being the final product after prolonged boiling. Insoluble in water; readily and completely soluble in alcohol.

Determination.—Ignite 1 gm. carefully to Fe_2O_3 after moistening with one or two drops of nitric acid. The commercial salt does not as a rule correspond with the above formula, but contains from 22 to 28 per cent. of Fe_2O_3.

Arsenic.—On 2 gm., as given under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferrous Ammonium Sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$=392·1. (Fe, 14·24; SO_4, 48·99; NH_3, 8·69; H_2O, 27·57.)—Solubility in water, 29; insoluble in alcohol.

Determination of Ammonia.—On 2·5 gm., as under Ammonium Sulphate. 1 cc. *N*/2 HCl ≡ 0·09804 gm. $FeSO_4.(NH_4)_2SO_4.6H_2O$.

Iron.—On 1 gm., as under Ferrous Sulphate. 1 cc. *N*/10 $KMnO_4$ ≡ 0·03921 gm. $FeSO_4.(NH_4)_2SO_4.6H_2O$.

Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4$ × 1·680 = $FeSO_4.(NH_4)_2SO_4.6H_2O$.

Common Impurities.—As under Ferrous Sulphate.

Arsenic.—On 5 gm., as under Ferrous Sulphate. Limit, 5 parts per million.

Ferrous Arsenate.—Ferrous arsenate, $Fe_3(AsO_4)_2.6H_2O$=553·5, with some ferric arsenate and iron oxide. A greenish, amorphous powder, insoluble in water, but readily soluble in hydrochloric acid.

Determination of Iron.—Titrate 2·5 gm. which have been dissolved in dilute sulphuric acid and air-free water with *N*/10 permanganate solution

until pink. 1 cc. $N/10$ $KMnO_4 \equiv 0{\cdot}01845$ gm. $Fe_3(AsO_4)_2.6H_2O$. The B.P. 1898 requires not less than 12·5 per cent. of hydrated ferrous arsenate.

Arsenic Acid.—Dissolve 0·5 gm. in a mixture of 17 cc. of conc. hydrochloric acid and 33 cc. of water in a conical flask. Pass a rapid stream of sulphuretted hydrogen through the solution to saturation. Cork the flask and allow to stand two hours. Again pass sulphuretted hydrogen, and wash with water by decantation. Filter through a Gooch crucible, wash, dry at 105° C., and weigh as As_2S_5. $As_2S_5 \times 0{\cdot}4832 = As$. $As_2S_5 \times 1{\cdot}7841 = Fe_3(AsO_4)_2.6H_2O$.

Impurities.—The salt should be free from sulphates.

Ferrous Carbonate, Saccharated.—A greenish-brown powder consisting of ferrous carbonate with a small amount of ferric carbonate and glucose.

Determination.—Weigh 1 gm. and add to this 10 cc. of cold 50 per cent. phosphoric acid. Allow to stand for fifteen minutes with frequent stirring. Dilute to 70 cc. with water, and titrate with $N/10$ dichromate to potassium ferricyanide as an external indicator. 1 cc. $N/10$ $K_2Cr_2O_7 \equiv 0{\cdot}01158$ gm. $FeCO_3$. The B.P. requires not less than 50 per cent. of ferrous carbonate.

Arsenic.—On 2 gm., as given under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferrous Iodide, $FeI_2 = 309{\cdot}7$. (Fe, 18·03; I, 81·97.)—When freshly made is white, but usually is steel grey or reddish brown. Readily soluble in water.

Determination.—Dissolve 0·25 gm. in 20 cc. of water, and add 20 cc. of $N/10$ silver nitrate and 3 cc. of conc. nitric acid. Heat on the water bath until the precipitate has become yellow. Cool, add 2 cc. of ferric alum indicator, and titrate with $N/10$ thiocyanate solution. 1 cc. $N/10$ $AgNO_3 \equiv 0{\cdot}01548$ gm. FeI_2.

Ferrous Lactate, $FeC_6H_{10}O_6.3H_2O = 288{\cdot}0$. (Fe, 19·39; $C_6H_{10}O_6$, 61·84.) —Solubility in water, 2·5; almost insoluble in alcohol; easily soluble in solutions of alkali citrates.

Determination.—Ignite 2 gm. carefully and weigh the residue of Fe_2O_3 (theory 27·74 per cent.). $Fe_2O_3 \times 2{\cdot}9302 = FeC_6H_{10}O_6$; $Fe_2O_3 \times 3{\cdot}6072 = FeC_6H_{10}O_6.3H_2O$.

Common Impurities.—Sugar, ferric salts (no colour should be produced on adding potassium iodide to the aqueous solution and acidifying with hydrochloric acid), carbonate, chloride, and sulphate.

Ferrous Phosphate, $Fe_3(PO_4)_2.8H_2O = 501{\cdot}7$.—A mixture of hydrated ferrous phosphate with ferric phosphate and ferric oxide, prepared by precipitating a solution of ferrous sulphate with a solution of sodium phosphate. Insoluble in water and acetic acid; soluble in hydrochloric acid. The B.P. preparation (*Ferri Phosphas. Saccharatus*) contains about 20 per cent. of glucose, and is required to contain not less than 60 per cent. of ferrous phosphate [$Fe_3(PO_4)_2.8H_2O$].

Determination.—Treat 0·5 gm. of the substance with 10 cc. of cold 50 per cent. phosphoric acid for fifteen minutes, dilute to about 70 cc. with water, and titrate with $N/10$ potassium dichromate to potassium ferricyanide as external indicator. 1 cc. $N/10$ $K_2Cr_2O_7 \equiv 0{\cdot}01672$ $Fe_3(PO_4)_2.8H_2O$.

Arsenic.—2 gm. are treated as under Ferric Ammonium Citrate. Limit, 5 parts per million.

Ferrous Sulphate, $FeSO_4.7H_2O = 278{\cdot}0$. (Fe, 20·08; SO_4, 34·55; H_2O, 45·37.)—Solubility in water, 54; insoluble in alcohol.

Determination of Iron.—Dissolve 1 gm. in 25 cc. of very dilute sulphuric acid, and titrate with $N/10$ permanganate until pink. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·01519 gm. $FeSO_4$, or 0·02780 gm. $FeSO_4.7H_2O$. The B.P. requires not less than 97·5 per cent. of the hydrated salt, the U.S.P. 54·36 to 57·07 per cent. of the anhydrous salt.

Sulphate.—On 0·7 gm., as under Sodium Sulphate. $BaSO_4 \times 0{\cdot}6507 = FeSO_4$; $BaSO_4 \times 1{\cdot}191 = FeSO_4.7H_2O$.

Common Impurities.—Zinc, copper, etc., may be tested for as under ferric chloride after oxidising the iron with nitric acid. The absence of basic sulphates is shown by the compound forming a clear solution with water.

Arsenic.—Dissolve 5 gm. in 10 cc. of water, add 15 cc. of hydrochloric acid and stannous chloride solution until the yellow colour disappears, and distil 20 cc. Add a few drops of bromine to the distillate, remove excess of bromine with stannous chloride solution, and proceed as usual. Limit, 5 parts per million.

Lead.—A 5 per cent. aqueous solution should give no precipitate on standing after the addition of a few drops of sulphuric acid.

Exsiccated Ferrous Sulphate.—This is ferrous sulphate deprived of a portion of its water of crystallisation at 100° C. It is a greyish-white, amorphous powder. The B.P. requires that it shall contain not less than 77 per cent. (U.S.P., 80 per cent.) of pure anhydrous ferrous sulphate when determined with $N/10$ permanganate. 1 cc. $N/10$ $KMnO_4 \equiv 0{\cdot}01519$ gm. $FeSO_4$. It should be slowly but entirely soluble in water, and should answer to the other tests for the crystallised salt.

Ferrous Sulphide, $FeS = 87{\cdot}9$. (Fe, 63·53; S, 36·47.)—Should be entirely soluble in dilute hydrochloric acid.

Determination.—Warm 0·1 gm. with dilute hydrochloric acid, and pass the resulting gases through 30 cc. of $N/10$ iodine solution contained in a series of U-tubes. When the evolution of gas has ceased, titrate the residual iodine with $N/10$ thiosulphate. 1 cc. $N/10$ $I \equiv 0{\cdot}004396$ gm. FeS.

Hydriodic Acid, $HI = 127{\cdot}9$. (H, 0·79; I, 99·21.)—A colourless gas which is extremely soluble in water—the saturated solution at 0° C. contains about 96 per cent. by weight. The solution rapidly becomes coloured, due to the liberation of iodine; for medicinal use this is prevented by the addition of hypophosphorous acid, but this addition is prejudicial to its use as a reagent, where the presence of a little free iodine does not usually interfere.

Determination.—Dissolve 0·5 gm. in 50 cc. of water; add 50 cc. of $N/10$ silver nitrate, and titrate back with $N/10$ thiocyanate to ferric alum. 1 cc. $N/10$ $AgNO_3 \equiv 0{\cdot}01279$ gm. HI. The acidity may be determined as a check by titrating 1·5 gm., diluted with water, with $N/2$ sodium hydroxide to methyl red. 1 cc. $N/2$ $NaOH \equiv 0{\cdot}06396$ gm. HI.

Commercial Strengths.—Two strengths are usually sold for reagent purposes; the weaker has S.G. 1·5 and contains about 43 per cent. of acid; the stronger has S.G. 1·7, and contains about 57 per cent. of acid and 1 per cent. of hypophosphorous acid as a preservative.

Common Impurities.—Barium, calcium, sulphate, phosphate, sulphide. The solution should be clear and colourless.

Determination of Other Halogens.—Dilute about 1 cc. with water, precipitate with silver nitrate, treat the precipitate with 10 per cent. ammonia

solution, filter and acidify the filtrate with nitric acid; only a faint opalescence should be produced.

Non-volatile Matter.—10 gm. evaporated and gently ignited should leave not more than 1 mg. of residue. This does not apply, of course, to samples containing hypophosphorous acid.

Arsenic and Lead.—As under Hydrochloric Acid.

Hydrobromic Acid, HBr=80·93. (H, 1·25; Br, 98·75.)—A colourless gas, very soluble in water. The saturated solution at 0° C. has S.G. 1·78, and contains about 70 per cent. hydrobromic acid. The solution often contains a trace of free bromine.

Determination.—Dissolve 0·5 gm. in water, add 50 cc. of *N*/10 silver nitrate solution, and titrate back with *N*/10 thiocyanate to ferric alum. 1 cc. N/10 $AgNO_3 \equiv$ 0·008093 gm. HBr. The acidity may be determined as a check by titrating 1·0 gm. diluted with water with *N*/2 sodium hydroxide to methyl red. 1 cc. *N*/2 NaOH $\equiv$ 0·04047 gm. HBr.

Commercial Strengths.—Two solutions are in common use, the stronger one having S.G. 1·38 and containing about 40 per cent. of acid, and the weaker one having S.G. about 1·27 and containing 30 to 32 per cent. of acid. The diluted hydrobromic acid of the B.P. has S.G. 1·077 and contains 10 per cent. of acid.

Common Impurities.—Sulphate, phosphate, chloride, and sulphide. The solution should be clear and colourless.

Iodine.—Add a few drops of ferric chloride solution to about 5 cc. of the acid and shake with a little chloroform. On standing, the chloroformic layer should not become coloured.

Non-volatile Matter.—10 gm. evaporated and gently ignited should leave not more than 1 mg. of residue.

Arsenic and Lead.—As under Hydrochloric Acid.

Hydrochloric Acid, HCl=36·47. (H, 2·77; Cl, 97·23.)—A colourless gas, freely soluble in water; the saturated solution at 0° C. contains about 45 per cent. and has S.G. 1·23.

Determination.—Weigh about 1 gm. in a weighing bottle, dilute with 50 cc. of water, and titrate with *N*/2 NaOH to methyl red. 1 cc. *N*/2 NaOH $\equiv$ 0·01823 gm. HCl. As an alternative, or as a check, dissolve 0·15 gm. in water, add 50 cc. of *N*/10 silver nitrate solution and titrate back with *N*/10 thiocyanate to ferric alum. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·003647 gm. HCl.

Commercial Strengths.—The concentrated acid has S.G. 1·16, and contains 31·8 per cent. of HCl (B.P., 31·79 per cent.); the diluted acid of the B.P. contains 10 per cent. of HCl and has a S.G. of 1·048.

Sulphates.—Evaporate 50 cc. of the acid to a low bulk, dilute to the original volume, add 10 cc. of 10 per cent. barium chloride solution, and allow to stand twelve hours. No precipitate should be produced.

Iron.—Dilute 5 cc. with water, and add 5 cc. of potassium thiocyanate solution; no red coloration should be produced.

Free Chlorine.—Dilute 5 cc. with water, and add a little potassium iodide solution and starch paste; no blue coloration should be produced.

Non-volatile Matter.—This should be less than 0·01 per cent. on evaporation and gentle ignition.

Arsenic.—10 cc. with 2 drops of stannous chloride solution should be treated as usual. Limit, 5 parts per million. The acid sold as arsenic-free

should contain less than 0·1 part per million. For the electrolytic method the process for halogen salts should be used.

Lead.—By the acid method, using 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Hydrofluoric Acid, HF=20·0. (H, 5·05; F, 94·95.)

Commercial Strengths.—The acid usually used as a reagent is a solution in water of about 40 per cent. strength.

Determination.—Dilute 1 gm. with water in a platinum dish and titrate with N sodium hydroxide to phenolphthalein. 1 cc. N NaOH $\equiv$ 0·02 gm. HF.

Non-volatile Residue.—About 5 gm. should leave no residue on evaporation and gentle ignition.

Sulphate.—Evaporate 1 gm. on the water bath, treat the residue with water and test with barium chloride solution; no immediate precipitate should be obtained.

Silica.—Dilute 2 gm. to 10 cc. with water, and add a solution of potassium chloride; no precipitate should be obtained.

Properties.—Great care should be taken not to allow the acid or its vapours to come into contact with the skin. It is best stored in bottles made of hard paraffin or gutta-percha.

Hydrogen Peroxide, H_2O_2=34·02. (H, 5·94; O, 94·06.)

Commercial Strengths.—It is usually sold as a solution containing from 3 to 30 per cent. of H_2O_2, although more concentrated solutions can be obtained. The strength is usually described as the number of volumes of oxygen which can be evolved from one volume of the solution. A 10-volume solution (roughly 3 per cent.) yields on treatment with excess of potassium permanganate 20 volumes of oxygen, half the oxygen coming from the potassium permanganate.

Determination.—The B.P. method depends on vigorously shaking 2 cc. of the 10-volume strength in a brine-charged nitrometer with 4 cc. of copper ammonium sulphate solution (*vide* Appendix). The iodine method of determination is probably the best available. In this case mix 10 cc. (of 10-volume, or a proportionate volume of stronger solutions) with 40 cc. of dilute sulphuric acid (28 cc. conc. sulphuric acid diluted to 100 cc. with water) and dilute to 100 cc. Run 10 cc. of this mixture into 10 cc. of potassium iodide solution, allow to stand five minutes and titrate the liberated iodine with $N/10$ sodium thiosulphate solution. 1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·001701 gm. H_2O_2, or 0·558 cc. oxygen.

Non-volatile Residue.—Only a slight residue should remain on evaporation to dryness. The B.P. limit of 1 per cent. is unnecessarily high for peroxide of the present day.

Free Acid.—This may be determined by titrating 25 cc. with $N/10$ sodium hydroxide solution to methyl red. The B.P. requires not more than 2·5 cc. A better standard is the pH value, which should not be less than 3 for the "10-volume" solution.

Barium.—1 cc. diluted with water should give no precipitate on adding sulphuric acid and allowing to stand for twelve hours.

Hypophosphorous Acid, H_3PO_2=66·06. (H, 4·58; PO_2, 95·42.)—Is used as an aqueous solution containing about 30 per cent. of pure acid. S.G. about 1·136.

Determination.—Titrate 1 gm. with $N/2$ sodium hydroxide to methyl

red. 1 cc. $N/2$ NaOH $\equiv$ 0·03303 gm. H_3PO_2. Hypophosphorous acid may be determined by the dichromate method as follows: Dilute 5 gm. to 50 cc. with water, neutralise with sodium hydroxide to methyl red and add 10 per cent. lead acetate solution until no further precipitation occurs; this precipitates phosphites. Dilute to 100 cc., shake well and allow to settle. Pipette 20 cc. of the clear liquid into a 250 cc. flask, add 50 cc. of N dichromate and 10 cc. of conc. sulphuric acid, and heat on the water bath for an hour. Cool, and dilute to 250 cc. Pipette 50 cc., add 10 cc. of potassium iodide solution and titrate the liberated iodine with sodium thiosulphate solution. Carry out a blank experiment omitting the hypophosphorous acid. 1 cc. N $K_2Cr_2O_7 \equiv$ 0·01652 gm. H_3PO_2 (*cf.* Calcium Hypophosphite).

Common Impurities.—Alkali metals, other phosphorus acids, sulphate, oxalate.

Arsenic.—Heat 2 gm. with 2 gm. of potassium chlorate and 10 cc. of hydrochloric acid until excess of chlorine is removed. Dilute with 40 cc. of water, add 3 drops of stannous chloride solution, and proceed as usual. Limit, 5 parts per million. For the electrolytic method treat 2 gm. by the method for Hypophosphites (p. 33).

Lead.—By the general method on 7 gm. after neutralising with ammonia, with 2 gm. in the control solution. Limit, 10 parts per million.

Iodine, I=126·9.—Solubility in water, 0·034; in alcohol, 8; in glycerol, 1·2; in carbon bisulphide, 25; in ether, 35; in chloroform, 3·1.

Determination.—Weigh 0·3 to 0·4 gm. in a weighing bottle, dissolve in 5 cc. of potassium iodide solution, dilute to 50 cc. with water and titrate with $N/10$ arsenious acid solution (or sodium thiosulphate). 1 cc. $N/10$ $As_2O_3 \equiv$ 0·01269 gm. I.

Non-volatile Matter.—No appreciable residue should remain on gently warming in a porcelain crucible (U.S.P., 0·05 per cent.).

Water.—The solution in chloroform should be transparent.

Impurities.—Thoroughly shake about 0·5 gm. of the finely powdered substance with water, and filter. Test the filtrate for cyanides and other halogens as follows.

Cyanides.—Decolorise half the filtrate with sodium thiosulphate solution, add a few drops of ferrous sulphate solution, and a little sodium hydroxide, warm gently and acidify with hydrochloric acid. No blue colour should be produced.

Chlorine and Bromine.—Add a slight excess of silver nitrate to the other half of the filtrate and allow the precipitate to settle. Decant the liquid, shake the precipitate with 1 per cent. ammonia solution, filter, and acidify the filtrate with nitric acid. Only a slight opalescence should be produced.

Lead.—Dissolve the non-volatile matter from about 0·5 gm. in acetic acid, make alkaline with ammonia and add sodium sulphide solution. No darkening should be produced.

Iron, Fe=55·84.—Iron wire or filings for pharmaceutical purposes should have a low sulphur and phosphorus content.

Determination.—Dissolve 1 gm. in dilute sulphuric acid in which a little sodium carbonate has previously been dissolved in order to prevent oxidation. Dilute to 250 cc. with air-free water and immediately titrate 25 cc. with $N/10$ potassium permanganate. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·005584 gm. Fe.

Sulphur and Phosphorus.—Dissolve 1 gm. in 10 cc. of concentrated phosphoric acid by gently heating; no phosphine should be evolved. The solution should not give an immediate black precipitate with silver nitrate solution.

Arsenic.—Mix 0·05 gm. with 0·1 gm. of potassium chlorate and 11 cc. of hydrochloric acid. Boil until all the chlorine has been expelled, and then add stannous chloride solution until colourless. Distil 14 cc., add 50 cc. of water, a few drops of stannous chloride solution, and proceed as usual. Limit, 200 parts per million. In the electrolytic method 0·05 gm. may be treated by the general method.

Reduced Iron (Ferrum Redactum).—A fine, black powder free from large metallic particles.

Determination.—Weigh 1 gm. into a conical flask, and add 10 gm. of powdered mercuric chloride and 50 cc. of boiling water. Boil for five minutes, shaking frequently, dilute with air-free water, cool, and make up to 100 cc. Shake, allow to stand for a few minutes, filter, and immediately titrate 20 cc. of the filtrate with $N/10$ $KMnO_4$ after the addition of 20 cc. of dilute sulphuric acid. 1 cc. $N/10$ $KMnO_4 \equiv 0{\cdot}005584$ gm. Fe. The B.P. requires that not less than 80 per cent. of metallic iron shall be present.

Matter Insoluble in Hydrochloric Acid.—Treat 0·5 gm. with boiling hydrochloric acid as long as any iron dissolves. Filter, wash, ignite, and weigh. The B.P. requires not more than 1 per cent. of residue.

Sulphur.—0·1 gm. treated with 10 cc. of dilute HCl in a test-tube should not impart more than a faint brown colour to a strip of lead acetate paper held over the mouth of the tube.

Arsenic.—As under Iron in last paragraph. Limit, 200 parts per million.

Kaolin.—A white china clay which consists mostly of hydrated aluminium silicate. It contains, roughly, aluminium oxide, 40 per cent.; silica, 47 per cent.; and water, 13 per cent. It is a white or dirty white powder, insoluble in practically all solvents. No effervescence should occur on the addition of dilute hydrochloric acid.

Tests.—It should contain only traces of iron and not more than 15 per cent. of matter volatile at a red heat. The matter insoluble in dilute hydrochloric acid may be determined by boiling 1 gm. with 25 cc. of the acid for half an hour, filtering, igniting, and weighing the residue.

Kieselguhr.—A siliceous deposit, consisting of the frustules and fragments of diatoms. For pharmaceutical purposes it should be purified by boiling with dilute hydrochloric acid, washed with water, dried and heated to redness. In this way the impurities, such as organic matter, iron oxide, etc., which usually occur along with the deposit in the natural state, are removed. It is a bulky, white or pale grey powder, odourless, tasteless, and insoluble in all ordinary solvents.

Tests.—A quantity of the material boiled with five times its weight of water should yield a colourless and neutral solution, which on evaporation to dryness leaves no residue. Kieselguhr on ignition should not char or evolve any odour. 2 gm. boiled with hydrochloric acid should cause no effervescence; the solution should not respond to tests for sulphate and iron, and on evaporation of one half of the solution practically no residue should be obtained (0·5 per cent., U.S.P.).

Lead Acetate, $Pb(CH_3COO)_2.3H_2O=379{\cdot}3$. ($Pb$, 54·62; CH_3COO, 31·13; H_2O, 14·25.)—It loses its water of crystallisation at 40° C., whilst at temperatures above 100° C. it is converted into a basic salt with loss of acetic acid. If the solution in water is not perfectly clear the cloudiness should immediately disappear on the addition of a little acetic acid. Soluble in water (100 cc. water dissolve 54 gm. anhydrous salt at 25° C.); in alcohol, 2·6; in glycerin, 20.

Determination of Lead.—Dissolve 5 gm. in recently boiled water and dilute to 100 cc. Pipette 10 cc. with 50 cc. of $N/10$ oxalic acid into a 200 cc. flask, shake for five minutes, make up to the mark, filter, and titrate 100 cc. of the filtrate hot with $N/10$ potassium permanganate after acidifying with 10 cc. of dilute sulphuric acid. 1 cc. $N/10$ oxalic acid $\equiv$ 0·01626 gm. $Pb(C_2H_3O_2)_2$, or 0·01896 gm. $Pb(C_2H_3O_2)_2.3H_2O$.

Acetate.—A process for the determination of acetate is given under Potassium Acetate, but this determination is rarely necessary.

Common Impurities.—Silver, copper, iron, zinc, calcium, alkali metals, chloride, and sulphate. The precipitate with potassium ferrocyanide should be perfectly white.

Lead Carbonate, Basic, $2PbCO_3.Pb(OH)_2=775{\cdot}6$. ($Pb$, 80·1; CO_2, 5·67.)—Insoluble in water, soluble in nitric and acetic acids.

Determination of Lead.—Dissolve 0·5 gm. in dilute nitric acid in a covered beaker, filter, if necessary, into a porcelain dish, and add an excess of dilute sulphuric acid. Evaporate, first on the water bath, and then over a flame until white fumes are evolved. Cool, add a little water, stir, and allow to stand overnight. Filter, wash with 4 per cent. sulphuric acid, and finally with alcohol. Ignite the precipitate apart from the paper. $Pb=PbSO_4\times 0{\cdot}6831$. The salt, on heating to redness, should leave a residue of about 85 per cent. of lead oxide.

Carbonate.—This may be determined in some modification of the Schrötter apparatus, using dilute nitric acid as the solvent.

Common Impurities.—The salt should be almost entirely soluble in dilute nitric acid (not more than 1 per cent. insoluble, B.P.C.), and the acetic acid solution precipitated with sulphuretted hydrogen and filtered should not leave any residue on evaporation and ignition.

Other Heavy Metals.—Dissolve 1 gm. in dilute nitric acid, add excess of sodium hydroxide solution (until the precipitate is redissolved), precipitate the lead by means of sulphuric acid, and add ferrocyanide solution to the filtrate; no precipitate or colour should be obtained, showing absence of copper, iron, and zinc.

Lead Chromate, $PbCrO_4=323{\cdot}2$. (Pb, 64·11; CrO_4, 35·89.)—Insoluble in water; should be almost entirely soluble in nitric acid.

Tests.—This salt is usually used for combustions, and should therefore not evolve carbon dioxide on heating in oxygen; the test is carried out under the conditions of a combustion, using at least 10 gm. of material. On shaking with hot water, filtering, and evaporating the filtrate, less than 0·1 per cent. of residue should be obtained.

Lead Dioxide, $PbO_2=239{\cdot}2$. (Pb, 86·59.)—A dark brown, amorphous powder. Insoluble in water, soluble in nitric acid.

Determination.—Treat 0·5 gm. with 1 gm. of potassium iodide, 25 gm of sodium chloride, 100 cc. of water, and 20 cc. of hydrochloric acid in a stoppered flask for five minutes. Titrate the liberated iodine with $N/10$ sodium

thiosulphate to starch. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}01196$ gm. PbO_2. Not less than 90 per cent. of PbO_2 should be present.

Impurities.—Chloride, manganese, alkali metals.

Manganese may be detected by boiling 2 gm. with 5 cc. nitric acid and 1 cc. of water. After diluting and precipitating the lead with sulphuric acid the filtrate should not be coloured pink.

Lead Iodide, PbI_2=461·0. (Pb, 45·00; I, 55·00.)—Solubility in cold water, 0·06, in boiling water, 0·4, giving rise to a colourless solution, from which the iodide separates out in golden scales on cooling; entirely soluble in solutions of acetates, alkali potassium iodide, and ammonium chloride.

Determination.—If necessary, the determination of lead and iodide may be carried out on warm, dilute aqueous solution in the usual way.

Common Impurities.—Nitrate and acetate. Lead chromate should be absent, as shown by complete solubility in ammonium chloride. Soluble impurities may be detected by precipitating the lead with sulphuretted hydrogen and evaporating the filtrate.

Lead Nitrate, $Pb(NO_3)_2$=331·2. (Pb, 62·56; NO_3, 37·44.)—Solubility in water, 48; in alcohol, 0·04.

Determination.—Dissolve 0·4 gm. in water, filter, if necessary, into a porcelain basin, add an excess of dilute sulphuric acid, and proceed as under Lead Carbonate. $Pb=PbSO_4 \times 0{\cdot}6831$. $Pb(NO_3)_2=PbSO_4 \times 1{\cdot}0923$.

Common Impurities.—Copper, iron, zinc, alkali and alkaline earth metals, chloride, and sulphate. See Lead Carbonate. Many impurities will show themselves by a turbidity when the salt is dissolved in water.

Lead Oleate, $Pb(C_{18}H_{33}O_2)_2$=769·9. (Pb, 26·91; $C_{18}H_{33}O_2$, 73·09.)—A white, granular powder somewhat greasy to the touch, soluble in alcohol, ether, benzene, and oil of turpentine.

Determination.—1 gm. may be gently ignited and the residue weighed as PbO.

Common Impurities.—Free alkali and acetates.

Lead Oxide (Litharge), PbO=223·2. (Pb, 92·83; O, 7·17.)—Insoluble in water, soluble in acetic and nitric acids.

Determination.—On 0·5 gm. as given under Lead Carbonate. $PbO=PbSO_4 \times 0{\cdot}7361$. It should not lose weight on heating to a dull red heat.

Common Impurities.—Copper, iron, calcium, etc., chloride and sulphate. 2 gm. should be almost entirely soluble in 20 per cent. acetic acid without the evolution of gas; the solution may be used for the subsequent tests. These may be carried out as under Lead Carbonate.

Lithium Benzoate, C_6H_5COOLi=128·0. (Li, 5·42; C_6H_5COOH, 95·31.)—Soluble in water (38) to give a clear solution free from odour; solubility in alcohol, 7.

Determination.—On 2 gm. as given under Ammonium Benzoate. 1 cc. $N/2$ $HCl \equiv 0{\cdot}064$ gm. C_6H_5COOLi. $C_6H_5COOH \times 1{\cdot}0662=C_6H_5COOLi$.

Common Impurities.—Iron, calcium, aluminium, chloride and sulphate.

Other Alkali Metals.—As under Lithium Citrate.

Arsenic.—Heat 1 gm. in a porcelain dish until thoroughly charred, dissolve in 14 cc. of brominated hydrochloric acid, remove the excess of bromine with a few drops of stannous chloride solution, and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Lithium Bromide, LiBr=86·9. (Li, 7·99; Br, 92·01.)—Solubility in water, 170; soluble in alcohol and ether.

Determination.—Dissolve 0·5 gm. in 25 cc. of water, add 50 cc. of N/10 silver nitrate and dilute nitric acid, and titrate back with sodium thiocyanate to iron alum. 1 cc. N/10 $AgNO_3 \equiv$ 0·00869 gm. LiBr. Not less than 85 per cent. LiBr should be present.

Common Impurities.—Bromate and iodide (which may be tested for as under potassium bromide), sulphate and chloride.

Other Alkali Metals.—Add 5 cc. of hydrochloric acid and 5 cc. of chlorine water to 0·4 gm. of lithium bromide contained in a flat-bottomed flask of 50 cc. capacity, evaporate the mixture almost to dryness on the water bath, add 10 cc. of amyl alcohol and cautiously heat the mixture until the lower aqueous layer has evaporated. Then add 3 drops of hydrochloric acid and boil the solution for three minutes; the resulting insoluble residue, if any, when collected on a filter, washed with amyl alcohol and dried at 100° C., weighs not more than 0·002 gm. The removal of water from the amyl alcohol mixture is facilitated by passing a current of air through the hot solution.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. In the electrolytic process the method for halogen salts must be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Lithium Carbonate, Li_2CO_3=73·9. (Li, 18·82; CO_3, 81·18.)—Solubility in water, 1·2; almost insoluble in alcohol; soluble in acids with effervescence.

Determination.—Dissolve 0·35 gm. in 25 cc. of N/2 hydrochloric acid, and titrate back with N/2 NaOH to bromophenol blue. 1 cc. N/2 HCl $\equiv$ 0·01847 gm. Li_2CO_3.

Common Impurities.—Aluminium, iron, chloride, and sulphate.

Other Alkali Metals.—Add a slight excess of diluted hydrochloric acid to 0·2 gm. of lithium carbonate contained in a flat-bottomed flask of 50 cc. capacity; evaporate the mixture almost to dryness on the water bath; add 10 cc. of amyl alcohol and cautiously heat the mixture until the lower aqueous layer has evaporated. Then add 3 drops of hydrochloric acid, and boil the solution for three minutes. The resulting insoluble residue, if any, when collected on a filter, washed with amyl alcohol and dried at 110° C., weighs not more than 0·002 gm. The removal of the water from the amyl alcohol mixture is facilitated by passing a current of air through the hot solution.

Arsenic.—By the method for Carbonates on 2 gm. Limit, 5 parts per million.

Lead.—On 4 gm. with 2 gm. in the control. Dissolve in acetic acid and boil off the carbon dioxide, make alkaline with ammonia, and proceed as usual. Limit, 10 parts per million.

Lithium Chloride, LiCl=42·4. (Li, 16·37; Cl, 83·63.)—Solubility in water, 75; in alcohol, 18·8; also soluble in a mixture of alcohol and ether.

Determination.—Titrate 0·2 gm. with N/10 silver nitrate to potassium chromate. 1 cc. N/10 $AgNO_3 \equiv$ 0·00424 gm. LiCl.

Common Impurities.—These are enumerated under Lithium Carbonate.

Other Alkali Metals.—Take 0·2 gm., place it in a 50 cc. conical flask, add a few cc. of water and 2 drops of dilute hydrochloric acid. Proceed as under Lithium Carbonate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. In the electrolytic process the method for Halogen Salts must be used.

Lead.—By the general method on 4 gm. with 2 gm. in the control. Limit, 10 parts per million.

Lithium Citrate, $Li_3C_6H_5O_7.4H_2O$=281·9. (Li, 7·38; $C_6H_5O_7$, 67·08; H_2O, 25·54.)—Forms white, somewhat deliquescent crystals. Solubility in water, 61·2.

Determination.—Ignite 1 gm. and extract the residue with hot water. Pour off through a filter paper and re-ignite the residue. Add 25 cc. of *N*/2 sulphuric acid to the residue, pour off and wash with water. Again ignite the residue, if necessary, finally washing the filter paper thoroughly with water. Titrate the excess of acid with *N*/2 sodium hydroxide to bromophenol blue. 1 cc. *N*/2 $H_2SO_4 \equiv$ 0·047 gm. $Li_3C_6H_5O_7.4H_2O$. The B.P. requires not less than 98·5 per cent.

Arsenic.—Test 5 gm. by the general method, using 15 cc. of stannated hydrochloric acid. Limit, 2 parts per million.

Lead.—On 7 gm. by general method. Limit, 6 parts per million.

Other Alkali Metals.—Gently ignite 0·2 gm., extract with dilute hydrochloric acid, filter, wash and evaporate the filtrate and washings almost to dryness on a water bath; add 10 cc. of amyl alcohol and continue as under Lithium Carbonate.

Lithium Hippurate, $C_6H_5CONH.CH_2.COOLi$=185·0. (Li, 3·77; $C_6H_5.CONH.CH_2.COOH$, 96·76.)—Solubility in water, 40.

Determination.—On 2 gm., as given under Lithium Citrate. 1 cc. *N*/2 HCl $\equiv$ 0·0925 gm. $C_9H_7O_3NLi$.

Common Impurities.—As given under Lithium Citrate.

Arsenic.—As given under Lithium Benzoate on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 4 gm. with 2 gm. in the control. Limit, 10 parts per million.

Lithium Iodide, LiI=133·9. $LiI.3H_2O$=187·9. (Li, 5·19; I, 94·81.)—Solubility in water, 160 (hydrated salt).

Determination.—Dissolve 0·5 gm. in 25 cc. of water, add 50 cc. of *N*/10 silver nitrate solution, and titrate with *N*/10 thiocyanate to iron alum. 1 cc. N/10 $AgNO_3 \equiv$ 0·01339 gm. LiI.

Impurities.—Similar to Lithium Chloride (*supra*).

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 2 gm. with 1 gm. in the control. Limit, 10 parts per million.

Lithium Salicylate, $C_6H_4OH.COOLi$=144·02. ($C_6H_4OH.COOH$, 95·89; Li, 4·82.)—Solubility in water, 122 at 25° C.

Determination.—On 3 gm., as given under Lithium Benzoate. 1 cc. *N*/2 HCl $\equiv$ 0·0720 gm. $C_6H_4OH.COOLi$.

Impurities.—See Lithium Benzoate.

Arsenic.—On 2 gm. by the method given under Lithium Benzoate. Limit, 5 parts per million.

Lead.—2 gm. in 50 cc. of water should show no darkening with sodium sulphide.

Lithium Sulphate, $Li_2SO_4.H_2O$=128·0. (Li, 10·85; SO_4, 75·07; H_2O, 14·08.)—Soluble in water, 33; also soluble in alcohol.

Determination of Sulphate.—On 0·2 gm., as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}5482 = Li_2SO_4.H_2O$.

Common Impurities.—Iron, aluminium, alkali, and alkaline earth metals, and chloride.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—4 gm. by the general method with 2 gm. in the control. Limit, 10 parts per million.

Magnesium Borocitrate.—*Preparation.*—This substance is prepared by stirring a mixture of magnesium oxide (3 parts), powdered boric acid (3 parts), and powdered citric acid (10 parts) with distilled water (4 parts) to form a pasty mass. The mixture in a short time sets to form a hard mass; then it may be powdered or the paste may be spread on glass and then scaled off. It should be completely soluble in water.

Determination.—Ignite 1 gm.; thoroughly extract the residue with dilute hydrochloric acid, filter, wash, and make the filtrate neutral with ammonia. Complete the precipitation of the magnesium as phosphate as given under Magnesium Carbonate below. $Mg = Mg_2P_2O_7 \times 0{\cdot}2184$. The substance usually contains about 8 per cent. of magnesium.

Common Impurities.—Calcium and tartrate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Magnesium Carbonate (Light and Heavy).—A hydrated basic carbonate containing about four molecules of water of crystallisation and about three molecules of carbonate to one of hydroxide. Insoluble in water; soluble in acids with effervescence.

Varieties.—It is prepared in two varieties, known as *heavy* and *light*, the respective densities being about 3½ to 1. A rough test of the density can be carried out by placing 2 gm. in a 25 cc. stoppered cylinder, shaking down by tapping twenty-five times on the bench and reading off the volume; the light salt should occupy about 18 cc. and the heavy about 4 cc.

Determination.—Ignite 2 gm. at a full red-heat; the B.P. requires that a residue of 42 to 44 per cent. of pure magnesium oxide should remain; the U.S.P. at least 39·2 per cent. Dissolve 1 gm. of the residue from the ignition in 50 cc. of *N*/2 hydrochloric acid and titrate back with *N*/2 sodium hydroxide to bromophenol blue to a bluish-violet colour. 1 cc. *N*/2 HCl ≡ 0·01008 gm. MgO. The magnesium may be determined gravimetrically in the usual way as follows: Dissolve 0·5 gm. in dilute hydrochloric acid with precautions to prevent splashing. Filter if necessary, and wash. Add to the mixed filtrate and washings 2 or 3 gm. of ammonium chloride solution and then make just alkaline with ammonia. Add 20 cc. of a 5 per cent. sodium phosphate solution drop by drop with continual stirring, and then allow to stand fifteen minutes. Add 25 cc. of 10 per cent. ammonia, and allow to stand at least twelve hours. Filter, wash with 3 per cent. ammonia solution, dry, ignite apart from the paper, and weigh as $Mg_2P_2O_7$. $Mg_2P_2O_7 \times 0{\cdot}3621 = MgO$; $Mg_2P_2O_7 \times 0{\cdot}2184 = Mg$.

Solubility.—Not more than 0·5 per cent. should be soluble in water.

Common Impurities.—Copper, iron, aluminium, chloride, and sulphate.

Calcium.—The U.S.P. has the following method for calcium determina-

tion. Dissolve 4 gm. in 50 cc. of dilute hydrochloric acid, dilute with 400 cc. of water, and add 5 gm. of ammonium chloride, 50 cc. of 4 per cent. ammonium oxalate solution and a little bromophenol blue. Then add 3 per cent. ammonia drop by drop (over a period of twenty minutes) with continual stirring until the liquid is blue. Allow the solution to stand overnight. Filter and wash the precipitate. Dissolve the precipitate in warm dilute hydrochloric acid and wash the filter to about 400 cc. Precipitate the filtrate as before, omitting the ammonium chloride. Filter off the precipitate, wash, ignite with sulphuric acid and weigh as calcium sulphate. ($CaO = CaSO_4 \times 0{\cdot}4119$.) The U.S.P. does not allow more than 0·8 per cent. of CaO.

Arsenic.—Dissolve 2 gm. in 14 cc. of brominated hydrochloric acid, remove the excess of bromine with stannous chloride solution and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 20 parts per million.

Magnesium Chloride, $MgCl_2.6H_2O = 203{\cdot}3$. (Mg, 11·96; Cl, 34·88; H_2O, 53·16.)—Solubility in water, 54; ($MgCl_2$) in alcohol, 17.

Determination of Magnesium.—On 0·5 gm., as given under Magnesium Carbonate. $Mg_2P_2O_7 \times 1{\cdot}826 = MgCl_2.6H_2O$; $Mg_2P_2O_7 \times 0{\cdot}8553 = MgCl_2$.

Chloride.—Dissolve 0·5 gm. in 50 cc. of water, and titrate with *N*/10 silver nitrate to potassium chromate. 1 cc. *N*/10 $AgNO_3 \equiv 0{\cdot}010165$ gm. $MgCl_2.6H_2O$, or 0·00476 gm. $MgCl_2$.

Common Impurities.—Iron, barium, calcium, sulphate, phosphate.

Magnesium Glycerophosphate, $C_3H_5(OH)_2PO_4Mg = 194{\cdot}4$. (Mg, 12·51; $C_3H_5(OH)_2PO_4$, 87·49.)—A white, amorphous powder. 1 gm. should almost entirely dissolve, after standing, in 50 cc. of water, not more than 0·3 cc. of 10 per cent. glycerophosphoric acid being required to effect complete solution.

Determination.—Ignite 1 gm. at first gently and finally strongly to a white ash of magnesium pyrophosphate. $Mg_2P_2O_7 \times 1{\cdot}746 = C_3H_5(OH)_2PO_4Mg$.

Free Phosphoric Acid.—If completely soluble, no free phosphate is present. If incompletely soluble, see Ferric Glycerophosphate for a method of determination.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Magnesium Hypophosphite, $Mg(H_2PO_2)_2.6H_2O = 262{\cdot}5$. (Mg, 9·26; H_2PO_2, 49·56; H_2O, 41·18.)—Solubility in water, 20.

Determination.—Take 5 gm. and determine by the method given under Calcium Hypophosphite. 1 cc. *N* $K_2Cr_2O_7 \equiv 0{\cdot}0328$ gm. $Mg(H_2PO_2)_2.6H_2O$ or 0·0194 gm. $Mg(H_2PO_2)_2$.

Impurities.—It should answer to the tests given under Calcium Hypophosphite.

Magnesium Lactate, $MgC_6H_{10}O_6.3H_2O = 256{\cdot}5$. (Mg, 9·49; $C_6H_{10}O_6$, 69·44; H_2O, 21·07.)—Solubility in water, 3·3.

Determination.—Dissolve 1 gm. in 50 cc. of water and determine magnesium as given under Magnesium Carbonate. $Mg_2P_2O_7 \times 0{\cdot}2184 = Mg$; $Mg_2P_2O_7 \times 2{\cdot}302 = MgC_6H_{10}O_6.3H_2O$.

Common Impurities.—Iron, aluminium, calcium, chloride, and sulphate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the acid method on 4 gm. with 2 gm. in the control. Limit, 10 parts per million.

Magnesium Oxide, $MgO=40{\cdot}3$. (Mg, 60·32; O, 39·68.)—Solubility in water, 0·02; less soluble in hot water than in cold. It should dissolve without effervescence in dilute acids to give a clear solution.

Determination.—Dissolve 0·4 gm. in 50 cc. of $N/2$ hydrochloric acid, and titrate back with $N/2$ sodium hydroxide to bromophenol blue. 1 cc. $N/2$ $HCl \equiv 0{\cdot}01008$ gm. MgO. The magnesium in 0·5 gm. may be determined gravimetrically as given under Magnesium Carbonate on p. 80.

Loss on Ignition.—The B.P. limit is 1 per cent. The U.S.P. allows a maximum of 10 per cent. While the B.P. standard is practicable when the magnesia is freshly prepared, after a short period of storage under normal conditions the loss on ignition soon rises above 1 per cent., particularly in the case of the light variety; it should not, however, be more than 5 per cent. if reasonable care is taken to avoid undue exposure.

Solubility in Water.—Should not exceed 0·7 per cent.

Varieties.—The substance is prepared in two varieties known as *light* and *heavy*, the respective densities being about as 1 to 3·5. Place 2 gm. in a 25 cc. cylinder, shake down by tapping twenty-five times on the bench and note the volume. "Light" should occupy about 18 cc., "heavy" about 5 cc.

Common Impurities.—Copper, iron, aluminium, chloride, and sulphate.

Calcium.—This may be detected as given under Magnesium Carbonate, p. 80.

Arsenic.—Mix 2 gm. with 14 cc. of brominated hydrochloric acid, add 50 cc. of water, decolorise with 2 drops excess of stannous chloride solution and proceed as usual. B.P. limit, 5 parts per million. For reagent purposes the limit should be 1 part per million. In the electrolytic process the general method may be used.

Lead.—By the acid method on 3 gm. with 1 gm. in the control. Limit, 20 parts per million.

Magnesium Peroxide.—*Preparation.*—This substance is prepared by mixing 100 gm. of dilute hydrogen peroxide (3 volumes) with 5 gm. of magnesium oxide and allowing them to remain in contact for two days at the ordinary temperature with periodical shaking. The precipitate is filtered off and dried at 100° C. It consists of a mixture of magnesium peroxide and magnesium hydroxide. It should contain about 15 per cent. MgO_2. It is a white, odourless, and tasteless powder, insoluble in water. It is stable at 100° C., but loses all its available oxygen at 300° C.

Determination.—Dissolve 2 gm. of potassium iodide in 200 cc. of water; add 0·25 gm. of the magnesium peroxide and 25 cc. of dilute sulphuric acid. Allow to stand for fifteen minutes, and titrate the liberated iodine with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}0008$ gm. available oxygen=0·002817 gm. MgO_2. Commercial samples usually contain 4 to 6 per cent. of available oxygen.

Common Impurities.—Copper, iron, aluminium, chloride, sulphate, and phosphate.

Calcium.—This may be detected as given under Magnesium Carbonate.

Arsenic.—As for Magnesium Carbonate. Limit, 5 parts per million.

Lead.—Dissolve 4 gm. (2 gm. in the control) in excess of acetic acid, boil, make alkaline with ammonia and proceed as usual. Limit, 20 parts per million.

Magnesium Salicylate, $(C_6H_4OH.COO)_2Mg.4H_2O$=370·5. (Mg, 6·56; $C_6H_4OH.COOH$, 74·53; H_2O, 19·45.)—Readily soluble in water, 25; also soluble in alcohol.

Determination of Magnesium.—By gently igniting 2 gm. and weighing the residue. The salt with four molecules of water yields 10·88 per cent. MgO; that with three molecules, 11·44 per cent. MgO. The magnesium may be further precipitated and weighed as pyrophosphate, as given under Magnesium Carbonate. $Mg_2P_2O_7 \times 0{\cdot}2184 = Mg$; $Mg_2P_2O_7 \times 0{\cdot}3621 = MgO$.

Salicylic Acid.—Dissolve 1 gm. in 100 cc. of water, acidify with dilute sulphuric acid, and extract three times with ether. Allow the ether to evaporate spontaneously, or below 60° C., dry in a desiccator, and weigh. Theory for four molecules of water is 74·53 per cent.; for three molecules of water, 78·34 per cent.

Impurities.—Tests for impurities should be carried out as under Sodium Salicylate.

Magnesium Sulphate, $MgSO_4.7H_2O$=246·5. (Mg, 9·87; SO_4, 38·97; H_2O, 51·16.)—Colourless crystals. Six molecules of water of crystallisation are lost at 150° C.; the seventh is not lost below 220° C. Solubility in water, 104; insoluble in alcohol.

Determination of Magnesium.—On 0·6 gm. as given under Magnesium Carbonate. $Mg_2P_2O_7 \times 0{\cdot}2184 = Mg$; $Mg_2P_2O_7 \times 2{\cdot}2136 = MgSO_4.7H_2O$. The B.P. requires not less than 97·4 per cent.

Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4 \times 1{\cdot}056 = MgSO_4$; $BaSO_4 \times 0{\cdot}5157 = MgSO_4.7H_2O$.

Common Impurities.—Iron, zinc, calcium, sodium, and chloride.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 12 gm. with 2 gm. in the control. Limit, 5 parts per million.

Zinc.—2 gm. dissolved in 50 cc. of water and 5 cc. of acetic acid should show no opalescence with 2 cc. of potassium ferrocyanide solution.

Chloride.—2 gm. dissolved in 50 cc. of water and 5 cc. of dilute nitric acid should not give more than a faint opalescence on the addition of silver nitrate solution.

Manganese Chloride, $MnCl_2.4H_2O$=197·9. (Mn, 27·76; Cl, 35·83; H_2O, 36·41.)—Solubility in water, 180; soluble in alcohol; insoluble in ether. Forms pink, tabular crystals readily oxidising on exposure to air, becoming brown. The whole of the water of crystallisation is lost at 100° C.

Determination of Manganese.—Dissolve 0·5 gm. in 200 cc. of water, add 20 gm. of ammonium chloride, and precipitate with sodium phosphate and ammonia. Filter, wash, and dry the precipitate; ignite the filter paper separately and gently ignite precipitate to form manganese pyrophosphate. $Mn_2P_2O_7 \times 1{\cdot}394 = MnCl_2.4H_2O$.

Chloride.—Titrate 0·25 gm. with *N*/10 silver nitrate to potassium chromate. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·009895 gm. $MnCl_2.4H_2O$, or 0·006293 gm. $MnCl_2$.

Common Impurities.—Iron, zinc, calcium, and sulphate.

Alkali and Alkaline Earth Metals.—Dissolve 2 gm. in water, precipitate the manganese with ammonium sulphide, filter, evaporate the filtrate to dryness, and ignite gently; not more than 0·1 per cent. of residue should be obtained.

Iron.—1 gm. dissolved in 20 cc. of water, acidified with hydrochloric acid, boiled with 1 cc. of chlorine water, and cooled, should not show any red colour on adding thiocyanate solution.

Manganese Glycerophosphate, $C_3H_5(OH)_2PO_4Mn$=225·0. (PO_4, 42·24; Mn, 24·41; $C_3H_5(OH)_2$, 33·35.)—Solubility in water, 9.

Determination of Combined Phosphoric Acid.—Gently ignite 0·2 gm., dissolve in 10 cc. of conc. nitric acid and 20 cc. of water, and add 15 gm. of ammonium nitrate. Heat to 70° C., and add about 100 cc. of molybdate reagent which has been warmed. Stir well, and allow to stand in a warm place (*e.g.* on the top of the steam oven) for at least four hours. Filter, wash with 10 per cent. ammonium nitrate solution, and discard the washings. Dissolve the precipitate on the filter in 3 per cent. ammonia solution, keeping the volume of the washings well below 100 cc. Mix the washings together, nearly neutralise with hydrochloric acid (till the precipitate which is formed just redissolves), and then add 25 cc. of magnesia mixture drop by drop with constant stirring. Allow to stand ten minutes, add 25 cc. of 10 per cent. ammonia, and allow to stand twelve hours. Filter, wash with 3 per cent. ammonia solution, and dry. Ignite the precipitate apart from the paper as $Mg_2P_2O_7$. $Mg_2P_2O_7 \times 0{\cdot}8534 = PO_4$; $Mg_2P_2O_7 \times 0{\cdot}6379 = P_2O_5$.

Free Phosphoric Acid.—0·1 gm. dissolved in 2 cc. of water and 5 cc. of dilute nitric acid should give no precipitate with 5 cc. of ammonium molybdate solution after standing one hour in the cold. For determination, see Ferric Glycerophosphate.

Arsenic.—See Ferric Glycerophosphate.

Manganese Hypophosphite, $Mn(H_2PO_2)_2.H_2O$=203·1. (Mn, 27·05; H_2PO_2, 64·08; H_2O, 8·87.)—Consists of pale pink granules; solubility in water, 15; almost insoluble in alcohol.

Determination.—Dissolve 6 gm. in 80 cc. of water, and continue as given under Calcium Hypophosphite. 1 cc. $N\ K_2Cr_2O_7 \equiv$ 0·02539 gm. $Mn(H_2PO_2)_2.H_2O$.

Common Impurities.—Barium, calcium, carbonate, phosphate.

Arsenic.—On 1 gm. by the method for Ferric Hypophosphite. Limit, 10 parts per million.

Lead.—By the acid method on 4 gm. with 2 gm. in the control. Limit, 10 parts per million.

Manganese Peroxide, MnO_2=86·9. (Mn, 63·19; O, 36·81.)—Insoluble in water or alcohol; soluble in hydrochloric acid. The U.S.P. requires that 1 gm., digested with 2 gm. of oxalic acid, 20 cc. of water, and 3 cc. of sulphuric acid on the water bath for several hours shall dissolve completely.

Determination.—Dissolve 0·2 gm. in 50 cc. of $N/10$ oxalic acid and 3 cc. of sulphuric acid by heating on the water bath. Dilute with 100 cc. of hot water, and titrate back with $N/10$ potassium permanganate. 1 cc. $N/10\ H_2C_2O_4 \equiv$ 0·004347 gm. MnO_2.

Manganese Sulphate, $MnSO_4.4H_2O$=223·0. (Mn, 24·63; SO_4, 43·06; H_2O, 32·31.)—Forms colourless or pale rose crystals. The whole of the

water of crystallisation is lost at about 110° C. Solubility in water, 136; insoluble in alcohol.

Determination of Manganese.—On 0·5 gm., as given under Manganese Chloride. $Mn_2P_2O_7 \times 1{\cdot}571 = MnSO_4.4H_2O$.

Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}6468 = MnSO_4$; $BaSO_4 \times 0{\cdot}9590 = MnSO_4.4H_2O$; $BaSO_4 \times 0{\cdot}4115 = SO_4$.

Common Impurities.—Iron, zinc, calcium, chloride.

Alkalis and Alkaline Earths.—Dissolve 2 gm. in water, precipitate the manganese with ammonium sulphide, filter, evaporate the filtrate to dryness and ignite gently. Not more than 0·1 per cent. of residue should be obtained.

Iron.—See Manganese Chloride.

Reducing Substances.—10 gm. dissolved in 100 cc. of cold water and acidified with sulphuric acid should not decolorise more than 0·1 cc. of *N*/10 potassium permanganate.

Mercuric Chloride (Corrosive Sublimate), $HgCl_2 = 271{\cdot}5$. (Hg, 73·88; Cl, 26·12.)—Solubility in water, 5; in alcohol, 23; in ether, 6·3.

Determination of Mercury.—On 1 gm., as given under Mercury, Ammoniated. $HgS \times 0{\cdot}8622 = Hg$; $HgS \times 1{\cdot}167 = HgCl_2$.

Chloride.—On 0·4 gm. by titrating with *N*/10 silver nitrate to potassium chromate. 1 cc. *N*/10 $AgNO_3 \equiv 0{\cdot}01358$ gm. $HgCl_2$.

Non-volatile Residue.—The salt should be completely soluble in water and completely volatile on ignition, leaving not more than 0·1 per cent. of residue (U.S.P.).

Impurities.—The impurities may be tested for generally by precipitating a solution of 2 gm. in water with sulphuretted hydrogen, filtering and evaporating the filtrate to dryness. Only the merest trace of residue should be obtained.

Mercuric Cyanide, $Hg(CN)_2 = 252{\cdot}6$. (Hg, 79·41; CN, 20·59.)—Solubility in water, 12·5; in alcohol, 9; in glycerin, 26; very slightly soluble in ether.

Determination of Cyanide.—Dissolve 0·3 to 0·4 gm. in 50 cc. of cold water, add 2 gm. of potassium iodide to the solution and titrate with *N*/10 hydrochloric acid to bromophenol blue until yellow. 1 cc. *N*/10 $HCl \equiv 0{\cdot}01263$ gm. $Hg(CN)_2$.

Mercury.—See Mercury, Ammoniated.

Non-volatile Residue.—The salt should be entirely volatile on gentle ignition.

Halogens.—A 5 per cent. solution of the salt acidified with nitric acid should give no turbidity with silver nitrate solution.

Mercuric Iodide, $HgI_2 = 454{\cdot}4$. (Hg, 44·14; I, 55·86.)—A bright red powder, insoluble in water, but soluble in aqueous solutions of mercuric chloride or potassium iodide. Solubility in alcohol, 0·3; in ether, 1·4. The red colour changes to yellow on heating to about 150° C., but returns on cooling.

Determination.—Dissolve 1 gm. in dilute hydrochloric acid, and proceed as under Mercury, Ammoniated. $HgS \times 0{\cdot}8622 = Hg$; $HgS \times 1{\cdot}953 = HgI_2$. The U.S.P. requires not less than 99 per cent. HgI_2 after drying.

Mercurous Iodide.—The salt should be entirely soluble in ether (absence of HgI).

Impurities.—Shake 1 gm. with 10 cc. of cold water, and filter. The

filtrate should only give the faintest reactions with sulphuretted hydrogen and silver nitrate respectively.

Non-volatile Residue.—Not more than 0·2 per cent. should be found (U.S.P.).

Mercuric Oxide, HgO=216·6. (Hg, 92·61; O, 7·39.)—Insoluble in water, soluble in hydrochloric or nitric acids.

Varieties.—Two varieties occur called respectively *yellow* mercuric oxide and *red* mercuric oxide (red precipitate); the former is prepared by precipitation with sodium hydroxide, and is very finely divided, the latter by heating mercurous nitrate, and occurs in small red crystals or as an orange-red powder. When treated with a 10 per cent. oxalic acid solution the red oxide is unchanged whilst the yellow oxide is converted into white mercuric oxalate.

Determination.—The B.P. recommends that the mercury be estimated as follows: "The solution obtained by dissolving 0·5 gm. in 2 cc. of nitric acid and diluting with 20 cc. of water requires not less than 45·8 cc. of *N*/10 solution of ammonium thiocyanate to produce a permanent pink coloration, solution of ferric sulphate being used as indicator." 1 cc. *N*/10 $NH_4CNS \equiv$ 0·01083 gm. HgO. The mercury may also be determined on 1 gm., as given under Mercury, Ammoniated. $HgS \times 0{\cdot}8622 = Hg$; $HgS \times 0{\cdot}9310 = HgO$. The B.P. standard corresponds to 99·2 per cent. HgO. The U.S.P. requires not less than 99·5 per cent. HgO after drying at 150° C.

Non-volatile Residue.—The B.P. requires not more than 0·3 per cent. for the red, and not more than 0·5 per cent. for the yellow variety; the U.S.P. standard for the latter is not more than 0·2 per cent.

Common Impurities.—Nitrate and chloride.

Mercuric Oxycyanide, $HgO.3Hg(CN)_2$=974·4. (Hg, 82·35; CN, 16·02.)—A white, crystalline powder, slightly soluble in water. The commercial salt varies in composition from almost pure cyanide to pure oxycyanide.

Determination.—Dissolve 0·5 gm. of the salt in 50 cc. of cold water, add 1 gm. of sodium chloride, and titrate with *N*/10 hydrochloric acid to bromophenol blue until yellow. 1 cc. *N*/10 HCl ≡ 0·01083 gm. HgO. 2 gm. of potassium iodide are then added to the solution, and the blue liquid is again titrated with *N*/10 hydrochloric acid as before. 1 cc. *N*/10 HCl ≡ 0·01263 gm. $Hg(CN)_2$. The salt should contain from 20 to 22 per cent. of HgO.

Non-volatile Matter.—Only a trace of residue should remain on ignition.

Halogens.—A nitric acid solution of the salt should give only the very faintest turbidity with a solution of silver nitrate.

Mercuric Oxysulphate (Turpeth Mineral), $HgSO_4.2HgO$=729·9. ($HgSO_4$, 40·65; HgO, 59·35; Hg, 82·45; SO_4, 13·16).—Insoluble in water, soluble in dilute acids.

Determination.—Dissolve 1 gm. in dilute hydrochloric acid, and proceed as under Mercury, Ammoniated. $HgS \times 0{\cdot}8622 = Hg$.

Common Impurities.—Iron and chloride.

Mercuric Salicylate, $C_6H_4.O.COOHg$=336·7. (Hg, 59·58; $C_6H_4.OH.COOH$, 41·00.)—A white, odourless powder; insoluble in water and alcohol, soluble in sodium hydroxide solution.

Determination.—Dissolve 0·3 gm. in 10 cc. of 10 per cent. sodium carbonate solution and add 1 gm. of potassium permanganate. After five minutes add carefully 5 cc. of concentrated sulphuric acid, and after a

further five minutes 40 cc. of water in small quantities. Add from 4 to 8 cc. of hydrogen peroxide solution until the precipitate is almost entirely dissolved, and then *N*/10 permanganate until a pink tint is just visible. Add a trace of ferrous sulphate solution to remove the pink colour. Titrate with *N*/10 thiocyanate to ferric alum. 1 cc. *N*/10 KCNS ≡ 0·01003 gm. Hg, or 0·01683 gm. C_6H_4.O.COOHg.

Tests.—The salt should not leave more than 0·2 per cent. of residue on ignition.

Mercurous Chloride (Calomel. Mild Mercurous Chloride, U HgCl=236·1. (Hg, 84·98; Cl, 15·02.)—Insoluble in water, alcohol, or eth...

Determination.—Treat 1 gm. in a stoppered flask with 10 cc. of water, 50 cc. of *N*/10 iodine, and 5 gm. of potassium iodide. Allow to stand with periodical shaking until solution is complete. Titrate back with *N*/10 sodium thiosulphate. 1 cc. N/10 I ≡ 0·02361 gm. HgCl. The U.S.P. requires not less than 99·6 per cent. after drying over sulphuric acid.

Non-volatile Residue.—The non-volatile residue should not exceed 0·1 per cent. (U.S.P.).

Mercuric Chloride.—1 gm. well shaken with water should give no reaction with sulphuretted hydrogen (absence of $HgCl_2$).

Impurities.—Treat 1 gm. with dilute nitric acid and evaporate to dryness. Dissolve the residue in dilute hydrochloric acid, precipitate the mercury with sulphuretted hydrogen, and evaporate the filtrate to dryness. Practically no residue should be obtained.

Ammonia.—When warmed with sodium hydroxide solution mercurous chloride becomes black, but no ammonia should be evolved.

Mercurous Iodide, HgI=327·5. (Hg, 61·25; I, 38·75.)—A yellow, amorphous powder, becoming green on exposure to light; insoluble in water, alcohol, or ether.

Determination.—Treat 1 gm. in a stoppered flask with 10 cc. of water, 50 cc. of *N*/10 iodine, and 5 gm. of potassium iodide. Allow to stand with periodical shaking until solution is complete. Titrate back with *N*/10 sodium thiosulphate. 1 cc. *N*/10 I ≡ 0·03275 gm. HgI.

Mercuric Iodide.—Treat 1 gm. of the material with alcohol, and filter. Dilute the filtrate with water and pass sulphuretted hydrogen; no precipitate should be obtained (absence of HgI_2).

Non-volatile Residue.—The non-volatile residue should not exceed 0·2 per cent.

Green Mercurous Iodide.—This is a mixture of mercurous iodide with traces of metallic mercury.

Mercurous Nitrate, $HgNO_3.H_2O$=280·6. (Hg, 71·48; NO_3, 22·10; H_2O, 6·42.)—Soluble in about twice its weight of water, but becoming turbid on dilution owing to the formation of basic salt.

Determination.—It is not advisable to determine mercury as sulphide. A suitable way is to treat 1 gm. with 25 cc. of 25 per cent. nitric acid, and add *N*/10 permanganate solution until the faintest permanent pink coloration is produced; the colour is removed by the aid of a little ferrous sulphate and the whole made up to 100 cc. 20 cc. are then titrated with *N*/10 ammonium thiocyanate solution, using ferric alum as indicator. 1 cc. *N*/10 thiocyanate ≡ 0·01303 gm. $HgNO_3$, H_2O.

Non-volatile Matter.—2 gm. should leave no appreciable residue on ignition.

Impurities.—Dissolve 1 gm. in about 10 cc. of water, acidify with 5 drops of 25 per cent. nitric acid, completely precipitate with hydrochloric acid, and filter. The filtrate should give only the slightest coloration with sulphuretted hydrogen, showing absence of mercuric salts.

Mercury, Hg=200·6.—Easily soluble in nitric acid; soluble in hot sulphuric acid with evolution of sulphur dioxide. S.G., 13·57; M.Pt., 38·8° C.; B.Pt., 357° C. At 15° C. the vapour pressure is equivalent to 0·033 mm. of mercury.

Tests.—10 gm. heated in a porcelain dish at a temperature below visible redness should leave not more than 0·02 per cent. of residue (U.S.P.). 5 gm. boiled with 5 cc. of water and 1 gm. of sodium thiosulphate should not lose its lustre, and should not acquire more than a slight yellow tinge.

Mercury, Ammoniated (Mercuric Chloroamide; " White Precipitate "), NH_2HgCl=252·1. (Hg, 79·57; Cl, 14·07; NH_2, 6·36.)—A white, heavy powder, insoluble in but slowly decomposed by water. On heating it should volatilise completely without fusing.

Determination.—*Sulphide Method.*[1]—Dissolve 1 gm. of the salt in a mixture of 75 cc. of water and 15 cc. of hydrochloric acid, dilute to 500 cc. and pass sulphretted hydrogen gas to saturation. Filter immediately through a Gooch crucible, wash well with water and finally with methylated spirit. Dry for two hours in the oven, and weigh. HgS×0·8622=Hg. Good commercial samples contain 77 to 79 per cent. of mercury. The U.S.P. requires 78 to 80 per cent. and the B.P. not less than 75·1 per cent.

The B.P. Method.—Triturate 0·3 gm. in a glass mortar with a few drops of water, transfer to a 300 cc. conical flask with the aid of 40 cc. of water, and finally rinse with a solution of 2 gm. of potassium iodide in 10 cc. of water and add the rinsings to the contents of the flask. Stopper the flask and rotate frequently until solution is complete. Titrate with *N*/10 hydrochloric acid to methyl red. 1 cc. *N*/10 HCl ≡ 0·0126 gm. NH_2HgCl.

Impurities.—It is difficult to obtain samples perfectly free from soluble chlorides without spoiling the colour. The best commercial samples always contain traces.

Mercury and Zinc Cyanide.—A white, amorphous powder, insoluble in water, probably an indefinite compound of mercuric and zinc cyanides. On careful ignition about 50 per cent. zinc oxide remains. Insoluble in water, soluble in dilute acids.

Determination.—Dissolve about 0·5 gm. in 20 cc. of dilute sulphuric acid, and dilute with 100 cc. of water. Add gradually 5 cc. of dilute hypophosphorous acid, and then 5 gm. of sodium chloride dissolved in 20 cc. of water. Stir thoroughly and allow to stand until the precipitate has subsided. Filter, and wash the precipitated mercury with distilled water. Transfer the precipitate to a flask, add 50 cc. of *N*/10 iodine and 2 gm. of potassium iodide, shake until the precipitate has dissolved and titrate the excess of *N*/10 iodine with *N*/10 thiosulphate. 1 cc. *N*/10 I ≡ 0·01003 gm. Hg., or 0·01263 gm. $Hg(CN)_2$. From 20 to 25 per cent. of mercuric cyanide should be present.

Molybdic Acid, H_2MoO_4=162·0; MoO_3=144·0.—Practically insoluble in water, easily soluble in ammonia and potassium hydroxide.

Determination.—Dissolve 0·5 gm. in dilute ammonia, make acid with acetic acid, and add excess of lead acetate solution. Allow the precipitate

[1] *Y.B.P.*, 1911, 445.

to stand, filter through a Gooch crucible, wash with hot water, dry, and ignite as $PbMoO_4$. $PbMoO_4 \times 0{\cdot}3921 = MoO_3$. Not less than 85 per cent. MoO_3 should be present.

Common Impurities.—Ammonia, chloride, sulphate.

Phosphates.—Dissolve 5 gm. in 20 cc. of 10 per cent. ammonia, and pour the solution obtained into 30 cc. of 30 per cent. nitric acid, warm slightly, and allow to stand. No yellow precipitate should be formed.

Heavy Metals.—The ammoniacal solution should not be darkened by the addition of ammonium sulphide solution.

Molybdic Anhydride should conform to the above tests and should contain not less than 99 per cent. MoO_3.

Nitric Acid, $HNO_3 = 63{\cdot}0$.—A strongly fuming liquid, colourless when pure, but usually slightly yellow due to the presence of oxides of nitrogen.

Commercial Strengths.—The liquid sold as concentrated nitric acid (S.G. 1·42) contains about 70 per cent. by weight of pure acid, whilst fuming nitric acid (S.G. 1·5) contains about 95 per cent. by weight of pure acid. The diluted nitric acid of the B.P. has S.G. 1·057, and contains 10 per cent. by weight of pure acid—10 cc. are officially required to neutralise 16·8 cc. of *N* sodium hydroxide. The acid of the U.S.P. contains from 67 to 69 per cent. HNO_3, and has S.G. 1·40 at 25° C.

Determination.—Weigh a weighing bottle containing 5 cc. of water, add 2 cc. of nitric acid, and weigh again. Wash out with 50 cc. of water and titrate with *N*/2 NaOH to methyl red. 1 cc. *N*/2 NaOH ≡ 0·03151 gm. HNO_3.

Residue on Evaporation.—10 cc., on evaporation and heating to 120° C., should not leave any appreciable residue. (U.S.P. requires not more than 0·015 per cent.)

Sulphate.—Evaporate 50 cc. to dryness with 0·1 gm. of sodium carbonate. Dissolve the residue in 50 cc. water, and add barium chloride solution. No precipitate should form in twelve hours.

Iodic and Bromic Acids.—Dilute with water, add a little zinc, and after a few moments shake with chloroform; on standing, the chloroform layer should not be coloured brown or violet.

Arsenic.—Heat 2 gm. with 2 cc. of strong sulphuric acid in a porcelain dish until white fumes are evolved. Cool, add 2 cc. of water, and again heat until white fumes are evolved. Cool, dilute with water, and proceed as usual.

Lead.—By the general method on 7 gm. with 2 gm. in the control, after neutralising the acid with ammonia. The B.P. limits are 20 parts of lead and 5 parts of arsenic per million, but for "reagent" acid, not more than 0·1 part of arsenic per million should be allowed.

Other Impurities.—Iron, calcium, chloride.

Perchloric Acid, $HClO_4 = 100{\cdot}5$.—*Commercial Strengths.*—The acid is usually sold as an aqueous solution containing about 20 per cent. of pure acid (S.G. 1·12). It should leave practically no residue on evaporation.

Determination.—The perchloric acid may be determined by precipitation as potassium perchlorate. For details, see Potassium Chloride. The acid may be also titrated with *N*/2 NaOH to thymol blue. 1 cc. *N*/2 NaOH ≡ 0·05023 gm. $HClO_4$.

Impurities.—The acid should be free from chlorides and sulphates and almost free from barium.

Heavy Metals.—About 2 cc., diluted with water, made alkaline with ammonia, and treated with sodium sulphide should show no darkening.

Phosphoric Acid, H_3PO_4=98·0.—*Commercial Strengths.*—The B.P. acid has S.G. 1·5, and contains 66·3 per cent. H_3PO_4. The U.S.P. acid has S.G. 1·75 and contains 85 to 88 per cent. H_3PO_4.

Determination.—Dissolve 1 gm. in 20 cc. of water, add 5 gm. of sodium chloride, and titrate with *N*/2 sodium hydroxide to phenolphthalein or to thymol blue to a blue colour. 1 cc. *N*/2 NaOH ≡ 0·0245 gm. H_3PO_4.

Common Impurities.—Calcium, chloride, nitrate, and sulphate.

Phosphite.—Dilute 1 cc. with water, add a little mercuric chloride solution, and warm. No opalescence should be produced.

Other Tests.—The diluted acid gradually added to a dilute solution of albumen should not produce any turbidity (absence of metaphosphoric acid). 5 cc. treated with 0·3 cc. of *N*/10 potassium permanganate and a little dilute sulphuric acid should remain coloured on heating to boiling.

Arsenic.—By the general method on 2 gm. B.P. limit, 5 parts per million; for reagent purposes 1 part per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control, after making alkaline with ammonia. Limit, 10 parts per million.

Phosphoric Acid, Glacial (Metaphosphoric Acid), HPO_3=80·05.—The acid occurs as deliquescent glassy lumps and sticks, readily soluble in water.

Tests.—After boiling with water (to convert it into the ortho acid) it should answer to the test given under Orthophosphoric Acid, except, of course, that for the absence of Metaphosphoric Acid.

Phosphorus, Yellow, P=31·04.—Insoluble in water; solubility in alcohol, 0·3; in olive oil, 1·2; in ether, 1·2; in chloroform, 4; in carbon bisulphide, 200. M.Pt., 44° C.; S.G., 1·8.

Sulphate.—1 gm. boiled with 20 cc. of 30 per cent. nitric acid should be dissolved without residue, the solution yielding not more than the slightest reaction for sulphate.

Potash, Sulphurated (*Potassa Sulphurata*, B.P., Liver of Sulphur).—A mixture of sulphides of potassium occurring as solid, greenish-yellow fragments, with an odour of hydrogen sulphide, and readily soluble in water.

Determination.—Dissolve 0·2 gm. in 10 cc. of water, add 5 cc. of sodium hydroxide solution and, slowly and with shaking, bromine solution, until excess of bromine is present. Acidify with hydrochloric acid, boil off the excess of bromine, and precipitate the sulphate with barium chloride in the usual way. S=$BaSO_4$×0·1374. The B.P. requires from 42 to 45 per cent. of sulphur.

Potassium Acetate, $CH_3.COOK$=98·1. (K, 39·86 per cent.; $CH_3.COOH$, 61·26 per cent.)—A very deliquescent substance, solubility in water, 243; in alcohol, 52·9. It usually contains up to 10 per cent. of water, which can be driven off at 110° C.

Determination of Potassium.—Ignite 1 gm. Treat the residue with water, filter, ignite residue, repeat the aqueous extraction, and titrate the combined filtrates with *N*/2 sulphuric acid to methyl red. 1 cc. *N*/2 H_2SO_4 ≡ 0·04907 gm. $KC_2H_3O_2$.

Acetate.—Distil about 1 gm. of the salt nearly to dryness with 10 cc. of a 40 per cent. phosphoric acid solution (free from volatile acids), add water, and repeat the distillation to remove the last traces of acetic acid.

The distillate is titrated with $N/2$ sodium hydroxide to phenolphthalein. 1 cc. $N/2$ NaOH ≡ 0·04907 gm. $KC_2H_3O_2$.[1]

Common Impurities.—Aluminium, calcium, iron, copper, magnesium, carbonate, sulphate, and chloride.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 12 gm. with 2 gm. in the control. Limit, 10 parts per million.

Potassium Bicarbonate, $KHCO_3$=100·1. (K, 39·06; CO_3, 43·96.)—Solubility in water, 31; insoluble in alcohol. The solubility is increased on boiling the solution owing to loss of carbon dioxide.

Determination.—Dissolve 1 gm. in water, and titrate with $N/2$ sulphuric acid to bromophenol blue. 1 cc. $N/2$ H_2SO_4 ≡ 0·05005 gm. $KHCO_3$. Alternatively, heat 1 gm. to redness (theoretical residue=68·98 per cent.), and titrate the residue in a similar manner.

Common Impurities.—Calcium, copper, iron, sulphate, chloride.

Arsenic.—On 2 gm., as under Potassium Carbonate. Limit, 2 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 5 parts per million.

Potassium Bisulphate, $KHSO_4$=136·2. (K, 28·72; H, 0·74; SO_4, 70·54.)—Occurs as opaque, white, hygroscopic lumps. Solubility in water, 50.

Determination.—Titrate 1·5 gm. with $N/2$ sodium hydroxide to bromophenol blue. 1 cc. $N/2$ KOH ≡ 0·0681 gm. $KHSO_4$. Gently ignite 1 gm., cool, treat with a few drops of conc. sulphuric acid, and ignite again strongly. The theoretical amount of residue is 63·99 per cent.

Potassium may be determined by the Perchlorate Method,[2] as given under Potassium Chloride, the sulphate being first removed.

Sulphates may be determined as given under Sodium Sulphate. $BaSO_4 \times 0{\cdot}4115 = SO_4$; $BaSO_4 \times 0{\cdot}5833 = KHSO_4$.

Common Impurities.—Chloride and iron.

Arsenic.—By the general method on 12 gm. with 2 gm. in the control, after making slightly alkaline with ammonia. Limit, 5 parts per million.

Heavy Metals.—1 gm. dissolved in 20 cc. of water and made alkaline with ammonia should not show any darkening with sodium sulphide solution.

Ammonia.—For reagent purposes not more than 15 parts per million of ammonia should be present, as determined on 1 gm. by adding 1 gm. of sodium hydroxide dissolved in 50 cc. of water, and testing with Nessler's reagent. The colour should not be deeper than that given by 1·5 cc. of ammonium chloride solution (1 cc. ≡ 0·01 mg. NH_3).

Potassium Bitartrate (Cream of Tartar), $KHC_4H_4O_6$=188·2. (K, 20·78; $C_4H_4O_6$, 78·68.)—Solubility in water, 0·45 (6·5 at 100° C.); insoluble in alcohol or ether.

Determination.—Dissolve 2 gm. in boiling water, and titrate with $N/2$ sodium hydroxide to phenol red to a red colour. 1 cc. $N/2$ NaOH ≡ 0·09408 gm. $KHC_4H_4O_6$. The determination may also be carried out by the method given under Potassium Citrate on 2 gm. 1 cc. $N/2$ HCl ≡ 0·09408 gm. $KHC_4H_4O_6$. The two methods should give identical results. The salt should show no loss on heating to 100° C.

[1] *Cf.* Gladding, *J. Soc. Chem. Ind.*, 1904, **23**, 350 and 530.
[2] *Cf.* Morris, *Analyst*, 1923, **48**, 250.

Common Impurities.—Copper, iron, calcium, magnesium, chloride, and sulphate.

Arsenic.—Dissolve 5 gm. in 50 cc. of water, add 13 cc. of brominated hydrochloric acid, and then stannous chloride solution until colourless, and proceed as usual. B.P. limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control, solution being effected by the addition of ammonia. Limit, 20 parts per million.

Potassium Bromide, KBr=119·0. (K, 32·85; Br, 67·15.)—Solubility in water, 62·5; in alcohol, 0·14.

Determination.—Dissolve 0·4 gm. in 25 cc. of water, add 50 cc. of *N*/10 silver nitrate, and titrate back with thiocyanate as usual. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·0119 gm. KBr.

Common Impurities.—Copper, iron, alkaline earths, carbonate.

Bromates and Iodides.—2 gm. dissolved in water, acidified with dilute sulphuric acid and shaken with chloroform, should not impart any colour to the chloroform layer on standing.

Thiocyanates and Iodides.—1 gm. in 10 cc. of water should give a pure yellow colour with ferric chloride solution (absence of thiocyanate), and on shaking this with a few drops of dilute sulphuric acid and a little chloroform only the slightest coloration of the chloroform should result (absence of iodides).

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Potassium Carbonate, K_2CO_3=138·2. (K, 56·58; CO_2, 31·84.)—The B.P. salt is a white, deliquescent, crystalline powder containing not less than 81·5 per cent. of pure K_2CO_3. The U.S.P. salt contains not more than 15 per cent. of water. There is also an exsiccated salt, which should contain not less than 95 per cent. K_2CO_3. Solubility in water, 109 (K_2CO_3); insoluble in alcohol.

Determination.—Dissolve 0·8 to 1·2 gm. (according to the degree of hydration) in water, and titrate with *N*/2 hydrochloric acid to bromophenol blue. 1 cc. *N*/2 HCl $\equiv$ 0·03455 gm. K_2CO_3. The B.P. salt should not lose more than 18·5 per cent. weight on heating to dull redness; the U.S.P. not more than 15 per cent. at 180° C.

Common Impurities.—Heavy metals, calcium, magnesium, sulphur compounds, chlorides, and sulphates.

Arsenic.—Dissolve 5 gm. in water, add 14 cc. of brominated hydrochloric acid, and then stannous chloride solution drop by drop until colourless, then proceed as usual. B.P. limit, 2 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 5 parts per million.[1]

Potassium Chlorate, $KClO_3$=122·6. (K, 31·9; Cl, 28·92; O, 39·18.)—Solubility in water, 6; in glycerin, 3·5; practically insoluble in alcohol, acetone, ether, or chloroform.

[1] For the action of potassium carbonate on lead glass, see Richmond, *Analyst*, 1923, 48, 260.

Determination.—Dissolve 0·25 gm. in 10 cc. of water and add 25 cc. of $N/10$ silver nitrate, 10 cc. of dilute nitric acid, and 5 cc. of 40 per cent. formaldehyde solution. Heat on a water bath until the precipitate has settled at the bottom, cool, dilute, and titrate the excess of silver with thiocyanate solution to ferric alum. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·01226 gm. $KClO_3$.

Common Impurities.—Iron, calcium, magnesium, nitrate, chloride, and sulphate.

Arsenic.—Dissolve 2 gm. in 10 cc. of water and 20 cc. of hydrochloric acid, warm to expel chlorine, then add stannous chloride solution, and proceed as usual. Limit, 5 parts per million. In the electrolytic method warm 2 gm. with 35 cc. of cadmiumated sulphuric acid until the chlorine is driven off, then proceed as usual.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Potassium Chloride, KCl=74·6. (K, 52·44; Cl, 47·56.)—Solubility in water, 34; in alcohol, 0·04.

Determination of Chloride.—Titrate 0·2 gm. with $N/10$ silver nitrate to potassium chromate. 1 cc. N/10 $AgNO_3 \equiv$ 0·007456 gm. KCl.

Potassium.[1]—[When sulphates are present the method of separation given under Potassium Sulphate must be used.] Weigh 0·2 gm. in a porcelain dish, add a little water and 5 cc. of a 20 per cent. perchloric acid solution. Evaporate on a hot plate until white fumes are copiously evolved. Dissolve the precipitate in water, add a little more perchloric acid solution and again concentrate to the fuming stage. Cool, stir the residue with 10 cc. of industrial methylated spirit. Filter through a Gooch crucible, drain well, and wash with 10 cc. of a 0·1 per cent. solution of perchloric acid in industrial methylated spirit two or three times. Dry at 130° C. and weigh. $KClO_4 \times 0{\cdot}2822 = K$; $KClO_4 \times 0{\cdot}5381 = KCl$.

Common Impurities.—Iron, sulphate, and chloride.

Calcium.—A 10 per cent. solution should give no precipitate with ammonium oxalate.

Chlorate.—A 10 per cent. solution should give no coloration with potassium iodide-starch solution.

Arsenic.—On 2 gm. by the general method. Limit, 5 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Potassium Chromate, K_2CrO_4=194·2. (K, 40·27; CrO_4, 59·73.)—Solubility in water, 62; insoluble in alcohol.

Determination.—Dissolve 0·15 gm. in water, add excess of potassium iodide and titrate the liberated iodine with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·006473 gm. K_2CrO_4. The solution of the salt should not give a green colour with thymol blue.

Common Impurities.—Sulphate and chloride.

Calcium, etc.—1 gm. dissolved in 20 cc. of water should give no precipitate with ammonia or ammonium oxalate solution.

Potassium Citrate, $K_3C_6H_5O_7.H_2O$=324·4. (K, 36·16; $C_6H_5O_7$, 59·22; H_2O, 5·55.)—A white, granular, deliquescent powder. The solution of the salt should not be alkaline to phenolphthalein. The whole of the water of crystallisation is lost at 200° C. Solubility in water, 162; practically insoluble in alcohol; soluble in glycerin.

[1] Morris, *Analyst*, 1920, **45**, 359; 1923, **48**, 250.

Determination.—Ignite 2 gm. until thoroughly charred, extract the residue with hot water, leaving the carbon in the dish to be ignited. Repeat until no carbon remains. Wash the filter-paper with hot water, and add 50 cc. of *N*/2 hydrochloric acid to the mixed filtrates. Titrate back with *N*/2 sodium hydroxide to bromophenol blue. 1 cc. N/2 HCl ≡ 0·05406 gm. $K_3C_6H_5O_7.H_2O$. The B.P. requires not less than 99 per cent. $K_3C_6H_5O_7.H_2O$. The U.S.P. requires the same percentage after drying over sulphuric acid.

Common Impurities.—Iron, calcium, magnesium, chloride, and sulphate.

Tartrate.—1 gm. of the salt dissolved in 1 cc. of water should give no precipitate on the addition of 1 cc. of acetic acid.

Arsenic.—By the general method on 5 gm., using 15 cc. of stannated hydrochloric acid. Limit, 2 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Potassium Cyanide, KCN=65·1. (K, 60·01; CN, 39·99.)—White lumps, with an odour of hydrocyanic acid. Solubility in water, 45; in alcohol, 0·8.

Determination.—Dissolve 0·5 gm. in 25 cc. of water, add 4 cc. of dilute ammonia, 3 drops of potassium iodide solution, and titrate with *N*/10 silver nitrate till a slight permanent precipitate appears. 1 cc. *N*/10 $AgNO_3$ ≡ 0·01302 KCN.

Commercial Strengths.—The salt occurs in commerce in varying strengths from 30 per cent. upwards, but it is quite possible to prepare samples containing 98 per cent. or more of potassium cyanide; salts for reagent purposes should contain at least 96 per cent. "*Double Salt*" is a double cyanide of sodium and potassium which contains cyanide equivalent to 98 to 100 per cent. of potassium cyanide. The "130 per cent." salt is a sodium salt containing cyanogen equivalent to 130 per cent. of potassium cyanide.

Sulphate.—A 1 per cent. solution should give no precipitate with barium chloride solution.

Ferrocyanide and Thiocyanate.—20 cc. of a 5 per cent. solution acidified with hydrochloric acid should not give a red or blue coloration with ferric chloride solution.

Chloride.—Mix 1 gm. in a porcelain dish with 2 gm. of potassium nitrate and 10 gm. of potassium carbonate and heat strongly. The residue, dissolved in water and acidified with nitric acid, should only give the faintest opalescence with silver nitrate.

Sulphide.—Lead acetate solution added to a 5 per cent. solution should give a perfectly white solution.

Potassium Dichromate, $K_2Cr_2O_7$=294·2. (K, 26·58; Cr, 35·35; O, 38·07.)—Solubility in water, 10; insoluble in alcohol.

Determination.—Dissolve 0·1 gm. in water, acidify with sulphuric acid, add 10 cc. of potassium iodide solution, and titrate the liberated iodine with *N*/10 sodium thiosulphate solution. 1 cc. *N*/10 $Na_2S_2O_3$ ≡ 0·004903 gm. $K_2Cr_2O_7$.

Impurities.—Calcium, chloride, sulphate.

Potassium Ferricyanide, $K_3Fe(CN)_6$=329·2. (K, 35·63; Fe, 16·96; CN, 47·41.)—Solubility in water, 40.

Determination.—Dissolve 0·7 gm. in 50 cc. of water, add 3 gm. of potassium iodide and 1·5 gm. of zinc sulphate free from iron, and titrate the

liberated iodine with $N/10$ thiosulphate solution. 1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·03292 gm. $K_3Fe(CN)_6$.

Impurities.—Sulphate and chloride should be absent. A crystal, well washed with water, the washings rejected, and dissolved in a further 50 cc. of water, should give no blue coloration with ferric chloride, showing absence of ferricyanide.

Potassium Ferrocyanide, $K_4Fe(CN)_6.3H_2O$=422·4. (K, 37·03; Fe, 13·22; CN, 36·95; H_2O, 12·80.)—Solubility in water, 22; insoluble in alcohol. The whole of the water of crystallisation is lost below 100° C.

Determination.—Dissolve 1 gm. in 200 cc. of water, add pure sulphuric acid, and titrate with $N/10$ potassium permanganate. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·04224 gm. $K_4Fe(CN)_6.3H_2O$.

Impurities.—The aqueous solution should be neutral. Carbonates and sulphates should be absent.

Chloride.—Dissolve 1 gm. in 10 cc. of water, precipitate with a slight excess of copper sulphate, and filter. The filtrate, acidified with nitric acid, should not show more than a faint opalescence with silver nitrate solution.

Potassium Formate, H.COOK=84·1. (K, 46·48; H.COOH, 54·72.)—Solubility in water, 330; soluble in alcohol; insoluble in ether. M.Pt. approximately 150° C.

Determination.—On 0·9 gm., as given under Calcium Formate. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·004205 gm. H.COOK.

Arsenic.—Weigh 2 gm. and thoroughly char in a porcelain dish. Treat the residue with 14 cc. of brominated hydrochloric acid and 50 cc. of warm water. Remove the excess of bromine with stannous chloride solution, and proceed as usual. Limit, 5 parts per million.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Potassium Glycerophosphate, $K_2PO_4.C_3H_5(OH)_2$=248·3. (K, 31·49; $C_3H_5(OH)_2$, 20·00; PO_4, 48·51.)—The 100 per cent. salt is rarely seen, the glycerophosphate commonly being used as a 50 or 75 per cent. solution. The solutions should be nearly colourless, and a 2 per cent. solution should not have a *p*H value greater than 10; the salt is soluble in all proportions in water. The 100 per cent. salt is very hygroscopic.

Determination.—Gently ignite 1 gm. to a white ash, and weigh as potassium pyrophosphate. $K_4P_2O_7 \times 1{\cdot}503 = K_2C_3H_7PO_6$. The salt may also be determined by dissolving 3 gm. in 50 cc. of water and titrating with $N/2$ HCl to methyl red to a maximum red colour (*p*H=4·4). 1 cc. $N/2$ HCl $\equiv$ 0·12415 gm. $K_2PO_4.C_3H_5(OH)_2$.

Impurities.—The examination for impurities may be carried out as for Sodium Glycerophosphate.

Potassium Hydroxide, KOH=56·1. (K, 69·69; OH, 30·31.)—Solubility in water, 107; soluble in alcohol. A 20 per cent. solution in water should be clear and colourless, whilst a 5 per cent. solution in alcohol should show only a small amount of deposit.

Commercial Qualities.—For commercial use this substance is sold both in powder and in flakes. For laboratory use three grades are distinguished —" pure," " pure by alcohol," and " A.R." The ordinary sticks contain about 80 per cent. of KOH, the " pure by alcohol " sticks about 85 per cent. The " A.R." is usually about the same strength as the " pure by alcohol," but is usually freer from silica, alumina, etc.

Determination.—Weigh 5 gm. in a weighing bottle and dissolve in about 100 cc. of recently boiled and cooled distilled water in a 250 cc. flask. Add 15 cc. of 10 per cent. barium chloride solution, dilute to the mark. Filter and titrate 50 cc. to phenolphthalein with *N*/2 hydrochloric acid. 1 cc. *N*/2 HCl ≡ 0·02805 gm. KOH.

Carbonate may be determined by titrating 1 gm. dissolved in about 50 cc. of water with *N*/2 hydrochloric acid to phenolphthalein. Let *m* equal number of cc. required. Then add bromophenol blue, and continue the titration until yellow. Let *n* equal number of cc. used. Then the amount of hydroxide is given by *m*—*n*, and the amount of carbonate by 2*n*. 1 cc. *N*/2 HCl ≡ 0·03455 gm. K_2CO_3.

Common Impurities.—Iron, aluminium, silica, sulphate, chloride, and nitrate. The best qualities should be almost free from chloride and sulphate. 5 gm. dissolved in acetic acid, a slight excess of ammonia added, and the whole diluted to 100 cc., should give no deposit of aluminium hydroxide on standing, nor should the solution be darkened on the addition of a few drops of ammonium sulphide solution, showing absence of iron. 5 gm. on solution in water and evaporation to dryness with excess of hydrochloric acid should give a clear solution free from any flocculent flakes of silica.

Nitrate.—1 gm. dissolved in 10 cc. of dilute sulphuric acid and 0·5 cc. of indigo solution added should remain blue on the addition of 10 cc. of conc. sulphuric acid.

Ammonia.—For reagent purposes not more than 10 parts per million of ammonia should be present. 1 gm. in 50 cc. of ammonia-free water should not give a deeper colour with 2 cc. of Nessler's reagent than 1 cc. of standard ammonium chloride. (1 cc. ≡ 0·01 mg. NH_3.)

Potassium Hypophosphite, KH_2PO_2=104·2. (K, 37·54; H_2PO_2, 62·46.)—Solubility in water, 160; in alcohol, 10. Very deliquescent.

Determination.—Dissolve 5 gm. in 50 cc. of water, add 10 cc. of lead acetate solution and dilute to 100 cc. Shake thoroughly and allow to stand for one hour. Pipette off 10 cc. and add 50 cc. of *N* potassium dichromate solution and 10 cc. of sulphuric acid, and heat the whole on the water bath for one hour. Dilute the liquid to 250 cc., pipette 25 cc., add 2 gm. of potassium iodide and titrate the liberated iodine with *N*/10 thiosulphate. A blank experiment omitting the hypophosphite should be carried out at the same time. 1 cc. *N* $K_2Cr_2O_7$ ≡ 0·02605 gm. KH_2PO_2.

Free Acid.—1 gm. dissolved in 10 cc. of water should not require more than 1·5 cc. of *N*/10 hydrochloric acid for neutralisation to methyl red (U.S.P.).

Phosphoric Acid.—1 gm. dissolved in water and tested with ammonia and magnesia mixture should give only the slightest precipitate.

Phosphorous Compounds.—5 cc. of a 20 per cent. solution mixed with 0·5 cc. of dilute hydrochloric acid, and heated on the water bath for half an hour should not develop any offensive odour.

Arsenic.—See Sodium Hypophosphite. Limit, 5 parts per million.

Lead.—Dissolve 4 gm. in acetic acid and use 2 gm., also dissolved in acetic acid, for the control. Neutralise with ammonia and continue as usual. Limit, 10 parts per million.

Potassium Iodate, KIO_3=214·0. (K, 18·27; I, 59·30; O, 22·43.)—Solubility in water, 6·3; insoluble in alcohol.

Determination.—Dissolve 1 gm. in water and dilute to 100 cc. Add

10 cc. of this solution to 20 cc. of potassium iodide solution containing 5 cc. of dilute hydrochloric acid, and titrate the liberated iodine with *N*/10 thiosulphate. 1 cc. *N*/10 $Na_2S_2O_3 \equiv$ 0·003567 gm. KIO_3.

Impurities.—No liberation of iodine should take place when a solution of the salt is mixed with a solution of potassium iodide. Sulphate, chloride, and iodide should be absent. The salt for reagent purposes should be of practically 100 per cent. purity.

Potassium Iodide, KI=166 0. (K, 23·13; I, 76·87.)—Solubility in water, 140; in ethyl alcohol, 6; in methyl alcohol, 13.

Determination.—Dissolve 0·7 gm. in 25 cc. of water, add 50 cc. of *N*/10 silver nitrate solution, 2 cc. of ferric alum indicator, and 2 cc. of dilute nitric acid; titrate back with *N*/10 ammonium thiocyanate solution. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·0166 gm. KI.

Impurities.—The aqueous solution should not be alkaline to phenolphthalein. The *p*H value of a 2 per cent. solution should be 7 to 9. 1 gm. dissolved in water should not give an immediate blue coloration with tartaric acid and starch solution. Sulphate should be absent.

Chloride and Bromide.—When 0·2 gm. is dissolved in 6 cc. of a 1 per cent. ammonia solution and 13 cc. of *N*/10 silver nitrate solution are added, the solution should give only a faint opalescence on shaking, filtering, and acidifying with nitric acid.[1]

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. In the electrolytic process the method for Halogen Salts must be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Potassium Metabisulphite, $K_2S_2O_5$=222·3. (K, 35·17; SO_2, 57·63.)—Soluble in water, slightly soluble in alcohol.

Determination.—Prepare a 0·5 per cent. solution, and run this from a burette into 50 cc. of *N*/10 iodine acidified with 10 cc. of dilute hydro chloric acid until colourless. 1 cc. *N*/10 iodine $\equiv$ 0 004446 gm. $K_2S_2O_5$.

Potassium Nitrate, KNO_3=101·1. (K, 38·67; NO_3, 61·33.)—Solubility in water, 26; in glycerin, 10; insoluble in alcohol.

Determination of Potassium.—This, if necessary, may be determined as under Potassium Chloride.

Nitrate.—Place 0·4 gm. in a porcelain dish, add 10 cc. of hydrochloric acid, evaporate to dryness on the water bath and repeat the process, continuing the second heating with the addition of a few drops of distilled water if necessary until all traces of free acid have been removed. Dissolve the residue in water and titrate with *N*/10 silver nitrate to potassium chromate. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·01011 gm. KNO_3. Should chloride be present in the original salt this must be determined separately by a blank titration, and the result subtracted from the above titration.

A more direct method is by reduction to ammonia. Place 1 gm. in a 500 cc. flask together with 50 cc. of water, 10 gm. of reduced iron[2] (this should be tested to see that it is unoxidised), and 20 cc. of sulphuric acid (S.G. 1·35), the flask being instantly closed with some kind of spray trap filled with glass beads. Boil the liquid for five minutes, rinse the beads into the flask, and boil for three minutes more. The reduction may also be carried out by the use of 20 cc. of 20 per cent. titanous chloride solution

[1] For the determination of bromides in iodides see Jones, *Y.B.P.*, 1921, 365.
[2] Devarda's alloy may be used with advantage, as under Bismuth Carbonate.

in alkaline solution. The solution is then distilled with excess of caustic soda, and the ammonia determined by receiving into standard acid as usual. 1 cc. $N/2$ HCl ≡ 0·05055 gm. KNO_3. A gasometric method, due to Crum and Lunge, can be carried out by dissolving about 0·4 gm. of the substance in less than 1 cc. of hot water, and transferring with the smallest possible quantity of water to a nitrometer (capable of holding some 130 cc.) filled with mercury. The nitrate is finally washed into the nitrometer with 10 to 15 cc. of conc. sulphuric acid, when the whole is thoroughly shaken until all evolution of gas has ceased. The apparatus is allowed to stand for a short time after the action has apparently ceased, when the volume of gas is read off and corrected to N.T.P. 1 cc. of NO at N.T.P. ≡ 0·004515 gm. KNO_3.

Common Impurities.—Copper, iron, calcium, magnesium, chloride, iodide, and sulphate.

Arsenic.—Heat 2 gm. with 2 cc. of sulphuric acid and 5 cc. of water until dense white fumes are evolved. Cool, add 3 cc. of water and again heat until white fumes are evolved. Cool, and proceed as usual. Limit, 5 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Potassium Nitrite, KNO_2=85·1. (K, 45·94; NO_2, 54·06.)—A colourless, deliquescent salt, very soluble in water, 300; slightly soluble in alcohol.

Determination.—Dissolve 0·2 gm. in 100 cc. of water containing 5 cc. of sulphuric acid, and add 50 cc. of $N/10$ potassium permanganate. Boil for a few minutes, cool, add excess of potassium iodide solution, and titrate the liberated iodine with $N/10$ thiosulphate. 1 cc. $N/10$ $KMnO_4$ ≡ 0·004255 gm. KNO_2.

Common Impurities.—Sulphate, chloride, and heavy metals.

Arsenic.—By the method given under Potassium Nitrate on 2 gm. Limit, 5 parts per million.

Lead.—Dissolve 5 gm. in 50 cc. of water, and add 5 cc. of dilute sulphuric acid. No precipitate should be obtained, B.P.

Potassium Oxalate, $K_2C_2O_4.H_2O$=184·2. (K, 42·45; C_2O_4, 47·77; H_2O, 9·78.)—Solubility in water, 33.

Determination.—Dissolve 0·25 gm. in 50 cc. of water, add 10 cc. of dilute sulphuric acid, warm, and titrate with $N/10$ permanganate. 1 cc. $N/10$ $KMnO_4$ ≡ 0·009212 gm. $K_2C_2O_4.H_2O$, or 0·008311 gm. $K_2C_2O_4$.

Common Impurities.—Chloride, sulphate, and heavy metals. 10 cc. of a 5 per cent. solution made alkaline with ammonia should show no darkening on the addition of sodium sulphide.

Potassium Perchlorate, $KClO_4$=138·6. (K, 28·22; Cl, 25·59; O, 46·19.)—Solubility in water, 1·6; in boiling water, 18; insoluble in alcohol.

Determination.—Mix 1 gm. of the powdered substance with 5 gm. of powdered sodium nitrate (free from chloride) in a nickel crucible, heat until fused, and keep in the fused condition for about half an hour. Cool, dissolve in water, and dilute to 200 cc. Take 100 cc. of this solution, add 50 cc. of $N/10$ silver nitrate, 20 cc. of nitric acid, and 5 cc. of ferric alum indicator, and titrate back with $N/10$ thiocyanate. 1 cc. N/10 $AgNO_3$ ≡ 0·01386 gm. $KClO_4$.

Common Impurities.—Chloride, sulphate, nitrate, and heavy metals.

Potassium Permanganate, $KMnO_4$=158·0. (K, 24·74; Mn, 34·76; O, 40·50.)—Solubility in water, 5.

Determination.—(1) Dissolve 0·790 gm. in water and make up to 250 cc. Place this solution in a burette, and titrate 25 cc. of $N/10$ oxalic acid diluted with 25 cc. of water, and acidified with 5 cc. of sulphuric acid. The number of cc. used divided into 2500 gives the percentage of potassium permanganate. 1 cc. $N/10$ oxalic acid ≡ 0·00316 gm. $KMnO_4$. (2) Dissolve 0·8 gm. in water, acidify with sulphuric acid, add excess of potassium iodide, and titrate the liberated iodine with $N/10$ thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3$ ≡ 0·003161 gm. $KMnO_4$. B.P. standard—not less than 99 per cent.; U.S.P. standard—not less than 99 per cent. after drying over sulphuric acid.

Common Impurities.—Heavy metals, chloride, sulphate, and nitrate. Impurities may be tested for by decolorising the solution with alcohol, and using the clear liquid.

Potassium Persulphate, $K_2S_2O_8$=270·3. (K, 28·93; S, 23·72; O, 47·35.)—Solubility in water, 3.

Determination.—Heat 0·5 gm. with 50 cc. of $N/10$ oxalic acid and 0·2 gm. of silver sulphate dissolved in 20 cc. of dilute sulphuric acid on the water bath until carbon dioxide is no longer evolved (15 to 20 minutes). Dilute the liquid to about 100 cc., and titrate the excess of oxalic acid with $N/10$ permanganate. 1 cc. $N/10$ $H_2C_2O_4$ ≡ 0·01352 gm. $K_2S_2O_8$.

Common Impurities.—Heavy metals and chloride.

Potassium Phosphate (Dipotassium hydrogen phosphate), K_2HPO_4= 174·2. (K, 44·88; H, 0·58; PO_4, 54·54.)—Occurs as crystalline masses or as a granular, deliquescent powder, very soluble in water. The *p*H value of a 1·2 per cent. solution should be 9·1.

Determination.—Dissolve 2·5 gm. in water, and titrate with $N/2$ hydrochloric acid to methyl red. 1 cc. $N/2$ HCl ≡ 0·08713 gm. K_2HPO_4. The process may be carried out gravimetrically as given under Sodium Phosphate. $Mg_2P_2O_7 \times 1{\cdot}565 = K_2HPO_4$; $Mg_2P_2O_7 \times 0{\cdot}8534 = PO_4$; $Mg_2P_2O_7 \times 0{\cdot}6379 = P_2O_5$.

Common Impurities.—Heavy metals, calcium, sulphate, chloride.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 5 parts per million.

Potassium Phosphate, Acid (Potassium dihydrogen phosphate), KH_2PO_4 =136·1. (K, 28·73; PO_4, 69·83.)—Forms large, colourless crystals, soluble to a clear solution in water. A solution of 0·9 per cent. strength should have a *p*H value of 4·5. The loss at 100° C. should not exceed 0·1 per cent.

Determination.—Dissolve 2 gm. in 200 cc. of water and titrate with $N/2$ NaOH to thymol blue to a blue colour (*p*H=9·2). 1 cc. $N/2$ NaOH ≡ 0·06805 gm. KH_2PO_4. For reagent purposes not less than 99·5 per cent. should be present.

Impurities.—Chloride and sulphate.

Arsenic and Lead may be tested for by the usual methods.

Potassium Salicylate, $C_6H_4OH.COOK$=176·2. (K, 22·19; $C_6H_4OH.COOH$, 78·37.)—Easily soluble in water and alcohol.

Determination.—This may be carried out as given under Sodium Salicylate, or as under Potassium Citrate. 1 cc. $N/2$ HCl ≡ 0·0881 gm. $KC_7H_5O_3$. $C_6H_4OH.COOH \times 1{\cdot}277 = C_6H_4OH.COOK$.

Free Salicylic Acid.—Dissolve 2 gm. in water, and titrate with $N/10$ sodium hydroxide to phenolphthalein. 1 cc. $N/10$ NaOH ≡ 0·01381 gm. $HC_7H_5O_3$.

Other impurities, arsenic and lead, may be tested for as given under Sodium Salicylate.

Potassium Sulphate, K_2SO_4=174·3. (K, 44·39; SO_4, 55·61.)—Solubility in cold water, 10; in boiling water, 26. The aqueous solution should be clear, and neutral to litmus. Insoluble in alcohol.

Determination.—Heat 1 gm. to redness with conc. sulphuric acid in a platinum crucible until constant in weight. The weight should be practically unchanged.

Potassium.—Gently ignite 0·2 gm., and then dissolve in about 80 cc. of water, add 10 cc. of hydrochloric acid, heat to boiling, and add a slight excess of boiling barium chloride solution. Allow to stand and filter as usual. (A trace of potassium is carried down in the precipitate—this may usually be disregarded, but it may be recovered if desired by igniting the barium sulphate, boiling with very dilute hydrochloric acid, filtering and adding the filtrate to the main solution.)[1] Evaporate the filtrate to dryness, dissolve the residue in a little water containing a few drops of hydrochloric acid, filter, wash, and evaporate to dryness. The process is then continued as under Potassium Chloride.

Sulphate.—On 0·5 gm., as given under Sodium Sulphate. $BaSO_4 \times 0·7466 = K_2SO_4$; $BaSO_4 \times 0·4115 = SO_4$. The B.P. requires that 1 gm. shall give 1·326 gm. of barium sulphate.

Common Impurities.—Iron, calcium, copper, magnesium, chloride, and nitrate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 4 gm. with 2 gm. in the control. Limit, 20 parts per million.

Potassium Tartrate, $(K_2C_4H_4O_6)_2.H_2O$=470·5. (K, 33·24; $C_4H_4O_6$, 62·93; H_2O, 3·83.)—Solubility in water, 138; soluble in alcohol.

Determination.—On 2 gm. by the method given under Potassium Citrate. 1 cc. *N*/2 HCl ≡ 0·05882 gm. $(K_2C_4H_4O_6)_2.H_2O$. The B.P. requires not less than 99 per cent.

Common Impurities.—Copper, iron, calcium, magnesium, chloride, and sulphate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 4 gm. with 2 gm. in the control. Limit, 20 parts per million.

Potassium Tetroxalate ("Potassium binoxalate," Salts of Lemon), $KH_3(C_2O_4)_2.2H_2O$=254·1. (K, 15·39; C_2O_4, 69·26; H_2O, 14·17.)—Solubility in water, 1·8.

Determination.—Dissolve 0·25 gm. in 50 cc. of water, add 5 cc. of sulphuric acid, warm, and titrate with *N*/10 permanganate. 1 cc. *N*/10 $KMnO_4$ ≡ 0·006354 gm. $KH_3(C_2O_4)_2.2H_2O$. Another method is to titrate with *N*/2 sodium hydroxide to phenolphthalein. 1 cc. *N*/2 NaOH ≡ 0·04236 gm. $KH_3(C_2O_4)_2.2H_2O$.

Impurities.—See Potassium Oxalate.

Potassium Thiocyanate, KCNS=97·2. (K, 40·24; CNS, 59·76.)—Forms colourless, deliquescent crystals. Solubility in water, 210; soluble in alcohol.

Determination—Dissolve 0·25 gm. in 50 cc. of water and 5 cc. of dilute nitric acid; titrate with *N*/10 silver nitrate, using ferric alum indicator. 1 cc. *N*/10 $AgNO_3$ ≡ 0·00972 gm. KCNS.

[1] Morris, *Analyst*, 1923, **48**, 255.

Common Impurities.—Heavy metals, ammonia, chloride, sulphate, ferrocyanide. The salt should be entirely soluble, giving a clear, colourless solution in water or alcohol.

Chloride.—Warm 1 gm. on a water bath with 100 cc. of water and 20 cc. of nitric acid until the odour of HCN is removed. On adding silver nitrate solution not more than a faint opalescence should be shown.

Prepared Chalk, $CaCO_3$=100·0. (Ca, 40·04; CO_3, 59·96.)—Insoluble in water, soluble in dilute acids with effervescence.

Determination.—As under Calcium Carbonate.

Preparation.—The substance is prepared from native calcium carbonate by grinding up with water, pouring off the milky fluid, and collecting the sediment that comes out on long standing. The U.S.P. requires it to contain not less than 97 per cent. of calcium carbonate, and also requires that not more than 2 per cent. shall be insoluble in dilute hydrochloric acid.

Barium.—1 gm. dissolved in dilute acetic acid should give no precipitate with potassium chromate solution.

Other Impurities.—As under Calcium Carbonate.

Silver Nitrate, $AgNO_3$=169·9. (Ag, 63·50; NO_3, 36·50.)—Solubility in water, 190; in alcohol, 3·8; slightly soluble in ether or glycerin.

Determination.—Dissolve 0·4 gm. in water, and titrate with *N*/10 thiocyanate in the presence of ferric alum and nitric acid. 1 cc. *N*/10 $NH_4CNS \equiv$ 0·01699 gm. $AgNO_3$.

Common Impurities.—Lead, copper, iron, sulphate. These may be tested for generally by dissolving 1 gm. in water, completely precipitating with hydrochloric acid, filtering, and evaporating the filtrate to dryness. No residue should remain.

Copper.—Dissolve 0·5 gm. in 5 cc. of water and add excess of ammonia; not the faintest blue coloration should be produced.

Silver Proteinate.—A number of compounds of silver with proteins are in use, known under various trade names. The compound usually known as silver proteinate is prepared from silver and partially hydrolysed gelatin. It is found as a brownish-yellow powder completely soluble in cold water. It contains about 8 per cent. of silver. No precipitation should occur on the addition of a dilute solution of sodium chloride. *Silver albuminate* contains about 10 per cent. silver, *silver nucleinate* from 18 to 20 per cent. silver, *silver vitellin* about 30 per cent. silver. Colloidal silver preparations such as *collargol* may contain from 50 to 80 per cent. silver.

Determination of Silver.—2 gm. of silver proteinate or 0·2 gm. of colloidal silver are heated with 20 cc. of conc. sulphuric acid and 4 cc. of concentrated nitric acid in a Kjeldahl flask until nitrous fumes are no longer evolved. After cooling, the solution is diluted with 25 cc. of water, the water is boiled off, and the heating continued for half an hour. The solution is then cooled, diluted with 100 cc. of water, ferric alum solution added, and the mixture titrated with *N*/10 thiocyanate. 1 cc. *N*/10 $NH_4CNS \equiv$ 0·01079 gm. Ag.

Sodium Acetate, $CH_3.COONa.3H_2O$=136·1. (Na, 16·90; CH_3COO, 39·72; H_2O, 43·38.)—Forms colourless crystals (hydrated) or pale grey masses (fused). The aqueous solution should be not more than slightly alkaline to phenolphthalein. The crystals melt completely at 75° C., and lose their water of crystallisation between 100° and 200° C. Solubility in water, 45; in alcohol, 7; in boiling alcohol, 60; insoluble in ether.

Determination.—On 1 gm., as given under Potassium Acetate. 1 cc. N/2 $H_2SO_4 \equiv$ 0·06804 gm. $CH_3.COONa.3H_2O$, or 0·041 gm. $CH_3.COONa$. The hydrated salt should contain 60 to 63 per cent. $NaC_2H_3O_2$, the fused salt not less than 99 per cent.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 4 gm. with 1 gm. in the control. Limit, 10 parts per million.

Sodium Arsenate, Na_2HAsO_4=186·0. (Na, 14·11; AsO_4, 85·27.)—A white powder. Solubility in water, 20; in alcohol, 1·8.

Determination.—Dissolve 0·25 gm. (0·5 gm. of the crystallised salt) in 25 cc. of water. Heat to 80° C., and add 10 cc. of hydrochloric acid and 3 gm. of potassium iodide; allow to stand for fifteen minutes at 80° C., cool, and titrate with *N*/10 sodium thiosulphate. 1 cc. *N*/10 $Na_2S_2O_3 \equiv$ 0·009299 gm. Na_2HAsO_4.[1]

The B.P. requires that the anhydrous salt shall not lose more than 2 per cent. on heating to 150° C.

Common Impurities.—Copper, iron, calcium, carbonate, chloride, sulphate, and nitrate.

Test for Arsenite.—Add 5 cc. of *N*/10 silver nitrate to 2 cc. of a 5 per cent. solution of the salt; no black precipitate of reduced silver should appear on boiling.

Lead.—By the general method on 2 gm.

Sodium Barbitone (Sodium diethylbarbiturate), $C_8H_{11}N_2O_3Na$=206·1. (Na, 11·16; $C_8H_{12}N_2O_3$, 89·33.)—Solubility in water, 17. A white, odourless powder.

Determination.—Dissolve 4 gm. in 50 cc. of water, add 25 cc. of ether and 50 cc. of *N*/2 hydrochloric acid, shake, and separate. Repeat the separation with three further quantities, each of about 20 cc. of ether. Mix the ethereal solutions, shake with 5 cc. of water, separate the latter and add it to the acid liquid. Titrate the acid liquid with *N*/2 sodium hydroxide to bromophenol blue to a bluish-violet colour. 1 cc. *N*/2 HCl $\equiv$ 0·10305 gm. $C_8H_{11}N_2O_3Na$. The mixed ethereal extracts may be evaporated to dryness, weighed, and tested as under Barbitone (p. 131).

Arsenic.—Heat 5 gm. in a porcelain dish until thoroughly charred, dissolve in 15 cc. of brominated hydrochloric acid and 50 cc. of hot water, remove the excess of bromine with stannous chloride solution and then proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Sodium Benzoate, $C_6H_5.COONa$=144·1. (Na, 15·96; C_6H_5COOH, 84·62.)—A white powder. Solubility in water, 50; in alcohol, 1·8. The "synthetic" salt should be without odour, the "natural" should have a faint odour of benzoin.

Determination of Sodium.—By igniting 1 gm. and titrating the residue with *N*/2 hydrochloric acid as given under Potassium Citrate. 1 cc. *N*/2 HCl $\equiv$ 0·07204 gm. C_6H_5COONa.

Benzoic Acid.—On 1·5 gm. by the process given under Ammonium Benzoate. $C_6H_5COONa = C_6H_5COOH \times 1·1802$. The B.P. requires not less than 96 per cent. of sodium benzoate.

[1] Corfield, Woodward, and Morris, *Y.B.P.*, 1921, 336 and 346.

The salt should not lose more than 4 per cent. on heating to 110° C. The aqueous solution should be practically neutral to phenolphthalein.

Common Impurities.—Copper, iron, potassium, chlorine compounds, sulphate, and carbonate.

Arsenic.—Heat 5 gm. in a porcelain dish until completely charred, and dissolve the residue in 14 cc. of brominated hydrochloric acid and 50 cc. of hot water. Add stannous chloride solution drop by drop until colourless and proceed as usual. Limit, 2 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Chlorine Compounds.—Test the benzoic acid obtained during the process of determination by the method given under Benzoic Acid (p. 132).

Sodium Bicarbonate, $NaHCO_3$=84·0. (Na, 27·38; CO_2, 52·37.)

Determination.—Dissolve 2 gm. in 30 cc. of water, add 50 cc. of *N*/2 HCl and titrate back with *N*/2 NaOH to bromophenol blue. 1 cc. *N*/2 HCl ≡ 0·04201 gm. $NaHCO_3$. The B.P. requires not less than 98·5 per cent., the U.S.P. not less than 99 per cent. when dry. On heating the salt above 100° C. the normal carbonate is formed, the bicarbonate losing 36·92 per cent. of its weight.

Common Impurities.—Copper, iron, calcium, ammonium, sulphite, thiosulphate, thiocyanate, chloride, and sulphate. The aqueous solution should not give a blue colour with thymol blue solution, showing absence of carbonate.

Arsenic.—By the method given under Sodium Carbonate. Limit, 2 parts per million.

Lead.—By the general method on 2 gm. with 2 gm. in the control. Limit, 5 parts per million.

Ammonia.—When heated in a dry test-tube the vapour should not be alkaline to litmus paper.

Sodium Bismuthate, $NaBiO_3$=280·0.—A yellowish-brown amorphous powder, insoluble in water. When 0·5 gm. is treated with 0·1 gm. of manganous sulphate and 10 cc. of 25 per cent. nitric acid a pink colour of permanganate is formed.

Determination.—Dissolve 0·5 gm. in 20 cc. of water and 20 cc. of hydrochloric acid. Add 5 gm. of potassium iodide and allow to stand for 30 minutes. Titrate the liberated iodine with sodium thiosulphate. 1 cc. N/10 $Na_2S_2O_3$ ≡ 0·014 gm. $NaBiO_3$; not less than 70 per cent. should be present.

Sodium Bisulphate, $NaHSO_4$=120·1. (Na, 19·15; SO_4, 79·97.)—The fused salt occurs as opaque, white, hygroscopic lumps, soluble in water, 30; insoluble in alcohol.

Determination.—Titrate 1·5 gm. with *N*/2 NaOH to methyl red. 1 cc. N/2 NaOH ≡ 0·06904 gm. $NaHSO_4.H_2O$ or 0·06004 gm. $NaHSO_4$.

Common Impurities.—Chloride and nitrate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Sodium Bisulphite, $NaHSO_3$=104·1.—Commercial sodium bisulphite consists of a mixture of sodium metabisulphite ($Na_2S_2O_5$), sodium sulphite, and sodium sulphate. It is a white, crystalline salt, soluble in water.

Determination of Total SO_2.—Add 0·25 gm. to a large beaker containing

50 cc. of $N/10$ iodine solution and 500 cc. of water. After stirring, titrate with $N/10$ thiosulphate. 1 cc. $N/10$ iodine $\equiv$ 0·003203 gm. SO_2. About 65 per cent. should be present.

SO_2 as Metabisulphite.—Pipette 10 cc. of "20-volume" hydrogen peroxide solution into each of three flasks containing 50 cc. of water coloured with bromophenol blue. Neutralise if necessary with $N/10$ NaOH. Add 1 gm. of the sample to each of two flasks. Shake and cool. Add 50 cc. of water to the "blank" and titrate the contents of the other flasks with $N/10$ NaOH until the colour is the same in all three flasks. 1 cc. $N/10$ NaOH $\equiv$ 0·009506 gm. $Na_2S_2O_5$.

Sulphate.—Boil 2 gm. with dilute hydrochloric acid until all sulphur dioxide is driven off. Precipitate with barium chloride in the usual way. $BaSO_4 \times 0{\cdot}6086 = Na_2SO_4$.

Thiosulphate.—The aqueous solution should not become turbid on acidification.

Sodium Bromide, NaBr=102·9. (Na, 22·35; Br, 77·65.)—Solubility in water, 87; in alcohol, 6; in ether, 0·08.

Determination.—Dissolve 0·4 gm. in 20 cc. of water, add 50 cc. of $N/10$ silver nitrate and titrate back with $N/10$ thiocyanate as usual. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·01029 gm. NaBr.

The salt should not lose more than 5 per cent. in weight when dried at 100° C.

Impurities.—Sodium bromide should be free from the impurities and answer the tests given under Potassium Bromide.

Sodium Cacodylate (Sodium dimethylarsenate), $Na(CH_3)_2.AsO_2$=160·0. (Na, 14·37; As, 46·84.)—A white, odourless, crystalline powder. Solubility in water, 200; in alcohol, 35. From 1 to 3·5 molecules of water of crystallisation may be present.

Determination of Acidity.—Titrate a solution of 2·5 gm. with $N/10$ aOH to thymol blue to a blue colour. Not more than 0·6 cc. should be re juired.

Neutral Salt.—The above solution is titrated with $N/2$ HCl to methyl red. 1 cc. $N/2$ HCl $\equiv$ 0·0800 gm. $Na(CH_3)_2AsO_2$. The U.S.P. requires from 72 to 75 per cent.

Water of Crystallisation.—The salt usually contains 15 to 30 per cent., all of which is lost at 120° C.

Monomethyl Arsenate.—10 cc. of a 5 per cent. solution of the salt should give no turbidity with calcium chloride solution.

Arsenate or Phosphate.—No precipitate should be obtained with magnesia mixture.

Common Impurities.—Heavy metals, chloride, and sulphate.

Sodium Carbonate, $Na_2CO_3.10H_2O$=286·2. (Na, 16·08; CO_2, 15·38; H_2O, 62 96.)—Solubility in water, 92; insoluble in alcohol. Three molecules of water of crystallisation are lost at about 35° C., nine molecules are lost at 70° C., whilst the salt becomes anhydrous at 100° C.

Determination.—Add 50 cc. of $N/2$ hydrochloric acid to 2·5 gm. of the salt; boil off the carbon dioxide, cool, and titrate back with $N/2$ sodium hydroxide to bromophenol blue. (1 cc. $N/2$ HCl $\equiv$ 0·07154 gm. Na_2CO_3 $10H_2O$.) In the case of the monohydrated salt $Na_2CO_3.H_2O$(=124·0) or the anhydrous salt Na_2CO_3(=106·0), 1 gm. should be taken for the titration. (1 cc. $N/2$ HCl $\equiv$ 0·03101 gm. $Na_2CO_3.H_2O$, or 0·02650 gm.

Na_2CO_3.) The B.P. requires the anhydrous salt to contain not less than 95 per cent. of sodium carbonate (Na_2CO_3).

Common Impurities.—Ammonia, copper, iron, calcium, sulphite, thiosulphate, thiocyanate, chloride, and sulphate.

Arsenic.—Dissolve 5 gm. in water, add 14 cc. of brominated hydrochloric acid and then stannous chloride solution drop by drop until colourless. Proceed as usual. Limit, 5 parts per million for the anhydrous salt, 2 parts per million for the crystalline salt.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit for the crystallised salt, 10 parts per million. On 3 gm. with 1 gm. in the control for the anhydrous substance. Limit, 25 parts per million.

Sodium Chloride, NaCl=58·46. (Na, 39·34; Cl, 60·66.)—Solubility in water, 35; in glycerin, 10; practically insoluble in alcohol or in ether.

Determination.—Titrate 0·25 gm. with *N*/10 silver nitrate to potassium chromate. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·005846 gm. NaCl. For reagent purposes not less than 99 per cent. should be indicated.

Common Impurities.—Iron, calcium, and sulphate.

Bromide and *Iodide.*—Extract 2 gm. thoroughly with warm alcohol, filter, and evaporate the filtrate to dryness. Dissolve the residue in water, add chlorine water and a little chloroform. The chloroform should show no coloration.[1]

Arsenic.—By the general method on 5 gm. Limit, 2 parts per million. In the electrolytic process the special method for Halogen Salts must be used.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Sodium Citrate, $Na_3C_6H_5O_7.2H_2O$=294·1. (Na, 23·46; H_2O, 12·24.)—Solubility in water, 100; practically insoluble in alcohol. The crystals effloresce in dry air and become anhydrous at 100° C.

Determination.—On 2 gm. as given under Potassium Citrate. 1 cc. *N*/2 HCl $\equiv$ 0·04902 gm. $Na_3C_6H_5O_7.2H_2O$, or 0·04335 gm. $Na_3C_6H_5O_7$. The aqueous solution should not be alkaline to phenolphthalein.

Common Impurities.—Carbonate, chloride, sulphate.

Tartrate.—Mix 1 gm. of powdered sodium citrate with 10 cc. of sulphuric acid in a test-tube previously rinsed with sulphuric acid, and maintain the temperature of the mixture at 90° C. for one hour; no colour darker than yellow should develop (absence of tartrate).

Arsenic.—By the general method on 5 gm., using 15 cc. of stannated hydrochloric acid. Limit, 2 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Sodium Cyanide, NaCN=49·0. (Na, 46·92; CN, 53 08.)—Solubility in water, 82; soluble in alcohol. Sodium cyanide crystallises from its aqueous solution, with two equivalents of water, in the form of flakes; at temperatures above 33° C. the anhydrous salt separates, which melts at 540° C.

Determination.—Dissolve 0·5 gm. in 25 cc. of water, add 4 cc. of dilute ammonia, 3 drops of potassium iodide solution, and titrate with *N*/10 silver nitrate to the production of a slight permanent precipitate. The percentage is usually expressed in terms of potassium cyanide for commercial purposes; thus sodium cyanide 120 per cent. contains 98 per cent. true NaCN. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·01303 gm. KCN, or 0·0098 gm. NaCN.

[1] For the determination of bromides in chlorides see Jones, *Y.B.P.*, 1921, 365.

Common Impurities.—For these and the methods for their detection see under Potassium Cyanide.

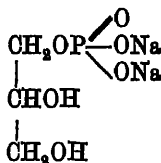
Sodium Formate, $H.COONa.2H_2O=104{\cdot}0$. (Na, 22·11; HCOO, 43·26; H_2O, 34·63.)—Solubility in water, 50; soluble in alcohol.

Determination.—Take 10 cc. of a 0·8 per cent. solution, add a 0·1 gm. of sodium carbonate and warm with 50 cc. of *N*/10 potassium permanganate for fifteen minutes on the water bath. Add 50 cc. of *N*/10 oxalic acid, then concentrated sulphuric acid until the liquid is clear, and titrate the excess of oxalic acid with *N*/10 permanganate. 1 cc. *N*/10 $KMnO_4 \equiv 0{\cdot}0034$ gm. H.COONa, or 0·0052 gm. $H.COONa.2H_2O$.

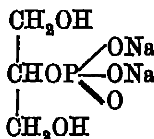
Arsenic.—Thoroughly char 2 gm. in a porcelain dish. Treat the residue with 14 cc. of brominated hydrochloric acid and 50 cc. of warm water. Remove the excess of bromine with stannous chloride solution and proceed as usual. In the electrolytic process the general method may be used. Limit, 5 parts per million.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Sodium Glycerophosphate, $C_3H_5(OH)_2PO_4Na_2=216{\cdot}1$. (Na, 21·28; PO_4, 43·98.)—The pure salt occurs in the form of colourless crystals, or as a fine, white powder. These crystals contain five molecules of water of crystallisation, and consist almost entirely of sodium β-glycerophosphate, the α-salt not being crystallisable.



Sodium α-glycerophosphate.



Sodium β-glycerophosphate.

The glycerophosphate is also met with as a pasty mass containing 75 per cent. of the anhydrous salt, and as a syrup of 50 per cent. strength. These forms of the substance consist chiefly of the α-salt. The 50 per cent. solution should not crystallise on standing in ice overnight.

Determination.—Ignite 1 gm. gently to a white ash of sodium pyrophosphate. $Na_4P_2O_7 \times 1{\cdot}625 = Na_2C_3H_7PO_6$.

Free Phosphate.—Dissolve 1 gm. of the salt in 50 cc. of water and place the solution in a burette. Take two Nessler cylinders each containing 10 cc. of 25 per cent. nitric acid and 10 cc. of 10 per cent. ammonium molybdate solution; to one cylinder add 5 cc. of a standard solution of phosphoric acid, 1 cc.=0·00004 gm. H_3PO_4, and to the second cylinder run in the solution from the burette. If no colour is produced by 10 cc. of the solution the phosphoric acid is less than 0·02 per cent. If the colour produced by 10 cc. of the solution is not as deep as the standard the phosphoric acid lies between 0·02 per cent. and 0·1 per cent., and the colour can be matched by taking less than 5 cc. of the standard solution. In this latter case the percentage of phosphoric acid$=n \times 0{\cdot}02$, where n is volume of the standard solution used. If the required volume of the solution lies between 1 and 10 cc. the percentage of phosphoric acid$=\frac{1{\cdot}0}{n}$, where n is the volume used from the burette. If less than 1 cc. of the solution is

required the solution should be diluted ten times and the determination repeated, the percentage of phosphoric acid being $\frac{10}{n}$, where n is the volume run in from burette.

Arsenic.—Thoroughly char 2 gm. in a porcelain dish. Dissolve the residue in 14 cc. of brominated hydrochloric acid and 50 cc. of water, add stannous chloride solution until colourless and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Sodium Hippurate, $C_6H_5.CO.NH.CH_2.COONa$=201·1. (Na, 11·44; $C_6H_5CO.NH.CH_2.COOH$, 89·06.)—Very soluble in water or alcohol.

Determination.—On 2·5 gm., as described under Potassium Citrate. 1 cc. $N/2$ HCl ≡ 0·1006 gm. $C_6H_5.CO.NH.CH_2.COONa$.

Arsenic.—Char 2 gm. in a porcelain dish. Dissolve in 14 cc. of brominated hydrochloric acid and 50 cc. of water, add stannous chloride solution until colourless and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 4 gm. with 2 gm. in the control. Limit, 10 parts per million.

Sodium Hydroxide, NaOH=40·0. (Na, 57·49; OH, 42·51.)—Solubility in water, 100; soluble in alcohol.

Commercial Qualities.—"Pure by alcohol" should contain not less than 95 per cent. of sodium hydroxide, and not more than 2·5 per cent. Na_2CO_3. The "pure stick" contains 90 to 95 per cent. sodium hydroxide. "Commercial" powder (so-called 98 to 99 per cent.) contains about 94 per cent., and "lump" contains upwards of 60 per cent. of hydroxide.

Determination.—Dissolve about 5 gm. (weighed in a weighing bottle) in 250 cc. of carbon dioxide-free water. Titrate 50 cc. of this solution with $N/2$ hydrochloric acid to phenolphthalein or thymol blue. Let N be the number of cc. used. Add bromophenol blue and continue the titration until yellow; let n=number of cc. used. N—n then corresponds to hydroxide and 2n to carbonate. 1 cc. $N/2$ HCl ≡ 0·0200 gm. NaOH or 0·0265 gm. Na_2CO_3. See also Potassium Hydroxide, p. 95.

Common Impurities.—Sulphate, chloride, and nitrate should be absent or practically so. 5 gm. on solution in water, and evaporation to dryness with excess of hydrochloric acid, should give a clear solution free from any flocculent insoluble matter, showing absence of silica. 5 gm. on dissolving in acetic acid, adding a slight excess of ammonia and diluting to 100 cc. should not deposit flakes of aluminium hydroxide on standing, nor should the solution be darkened by the addition of a few drops of ammonium sulphide solution, showing absence of iron. For reagent purposes it should not contain more than 10 parts of ammonia per million, as determined by Nessler's reagent, as under Potassium Bisulphate, p. 91.

Sodium Hypophosphite, NaH_2PO_2=88·0. (Na, 26·13; H_2PO_2, 73·87.)—Solubility in water, 108; soluble in glycerin; slightly soluble in alcohol; insoluble in ether.

Determination.—By the method given under Potassium Hypophosphite. 1 cc. N $K_2Cr_2O_7$ ≡ 0·0220 gm. NaH_2PO_2. The B.P. salt is anhydrous, containing not less than 97 per cent. of pure sodium hypophosphite, and is

l to lose not more than 2 per cent. of its weight when heated at

enic.—Mix 1 gm. of the salt with 2 gm. of potassium chlorate and
f hydrochloric acid and allow to stand for one hour. Warm to expel
of chlorine, add 40 cc. of water and a few drops of stannous chloride
and proceed as usual. Limit, 5 parts per million. In the electro-
ocess the method given for Hypophosphites (on p. 33) should be

d.—Dissolve 4 gm. in acetic acid and use 2 gm. for the control.
ise with ammonia and continue as usual. Limit, 10 parts per

ium Iodide, NaI=149·9. (Na, 15·35; I, 84·65.)—Solubility in water,
alcohol, 43; in glycerin, 100.
rmination.—Dissolve 0·5 gm. in 25 cc. of water, add 50 cc. of $N/10$
itrate, 2 cc. of ferric alum indicator, and 2 cc. of dilute nitric acid
ate back with $N/10$ ammonium thiocyanate. 1 cc. $N/10$ $AgNO_3 \equiv$
gm. NaI. The B.P. requires that it should not lose more than 5 per
its weight when dried at 110° C., and that the dried salt so obtained
indicate not less than 99 per cent. and not more than 101·6 per cent.
um iodide.
urities.—It should answer to the tests given under Potassium

ium Lactate, $C_3H_5O_3Na$=112·1. (Na, 20·52; $C_3H_5O_3$, 79·48.)—A
ss or slightly yellow, viscid liquid, neutral or slightly alkaline. Very
in water or alcohol; insoluble in ether.
rmination.—On 1·5 gm. as described under Potassium Citrate.
/2 HCl ≡ 0·05603 gm. $NaC_3H_5O_3$. The amount of carbonate present
original substances must be determined by titration and, if appreci-
lowed for in this titration.
nmon Impurities.—Carbonates, calcium, iron, chloride, and sulphate.
tic Acid.—The lactate should not evolve an odour of acetone on heat-
h tartaric acid.
lucing Sugars.—The aqueous solution should not be changed on
ng with ammoniacal silver nitrate solution.
cerin.—Mix 2 gm. of the substance with 3 gm. of zinc sulphate, warm
water bath, extract with a mixture of 2 parts of alcohol and 1 of
nd evaporate the solution to dryness. No residue should be obtained.
senic.—Char 2 gm. in a porcelain dish, dissolve the residue in 14 cc.
ninated hydrochloric acid and 50 cc. of water, add stannous chloride
n until colourless, and proceed as usual. Limit, 5 parts per million.
electrolytic process the general method may be used.
d.—By the general method on 4 gm. with 2 gm. in the control.
10 parts per million.

lium Metabisulphite, $Na_2S_2O_5$=190·1. (Na, 24·20; SO_4, 50·53.)—
y soluble in water.
paration.—Sodium metabisulphite is prepared by supersaturating a
n of sodium carbonate with sulphur dioxide; anhydrous crystals are
ed on cooling.
termination.—Prepare a 0·5 per cent. solution and run this from a
into 50 cc. of $N/10$ iodine acidified with hydrochloric acid. 1 cc.
≡ 0·003802 gm. $Na_2S_2O_5$.

Sodium Nitrate, $NaNO_3$=85·0. (Na, 27·06; NO_3, 72·94.)—Solubility in water, 84; in alcohol, 0·04.

Determination.—By the methods given under Potassium Nitrate. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·0085 gm. $NaNO_3$. 1 cc. $N/2$ $HCl \equiv$ 0·0425 gm. $NaNO_3$. 1 cc. of NO at N.T.P. $\equiv$ 0·003799 gm. $NaNO_3$.

Common Impurities.—Copper, iron, calcium, magnesium, potassium, chloride, iodide, and sulphate.

Arsenic.—Heat 2 gm. with 2 cc. of strong sulphuric acid until dense white fumes are evolved. Cool, add 3 cc. of water, and again heat until white fumes are evolved. Cool, add 50 cc. of water, and proceed as usual. Limit, 5 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million.

Sodium Nitrite, $NaNO_2$=69·0. (Na, 33·33; NO_2, 66·67.)—Solubility in water, 83; sparingly soluble in alcohol.

Determination.—By the method given under Potassium Nitrite. 1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·00345 gm. $NaNO_2$. Not less than 95 per cent. should be present.

Common Impurities.—Sulphate, chloride, heavy metals, calcium.

Arsenic.—On 2 gm., as under Sodium Nitrate above. Limit, 5 parts per million.

Lead.—Dissolve 5 gm. in 50 cc. of water and add 1 cc. of dilute sulphuric acid; no precipitate should be obtained on standing.

Sodium Nitroprusside, $Na_2Fe(CN)_5(NO).2H_2O$=297·9. (H_2O, 12·09.)—Solubility in water, 40.

Tests.—A 2 per cent. aqueous solution should show only a slight turbidity on adding hydrochloric acid and barium chloride. On adding a few drops of hydrogen sulphide solution to the 2 per cent. solution and making alkaline with a little sodium hydroxide, a purple-red colour should appear. Test for ferrocyanide with ferrous sulphate solution and for ferricyanide with ferric chloride solution.

Sodium Oxalate, $(COONa)_2$=134·0. (Na, 34·33; $(COO)_2$, 65·67.)—A white, crystalline powder. Solubility in water, 3.

Determination.—Titrate 0·2 gm. dissolved in 10 cc. of dilute sulphuric acid and 40 cc. of water, and warmed to about 60° C., with $N/10$ potassium permanganate. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·0067 gm. $Na_2C_2O_4$. Not less than 99·9 per cent. should be found.

Common Impurities.—Chloride, sulphate, and heavy metals.

Sodium Perborate, $NaBO_3.4H_2O$=154·0. (Na, 14·97; BO_3, 38·27; H_2O, 46·76.)—Solubility in water, 2·5.

Determination.—Dissolve 0·25 gm. in 50 cc. of water and run the solution into a mixture of 25 cc. of potassium iodide solution and 100 cc. of dilute hydrochloric acid, contained in a stoppered bottle. Stopper and allow to stand for half an hour. Titrate the liberated iodine with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·0077 gm. $NaBO_3.4H_2O$.

Tests.—1 cc. of a 2 per cent. solution, 1 cc. of dilute sulphuric acid, and a few drops of potassium chromate solution shaken with 2 cc. of ether will cause the ether to acquire a blue colour.

Common Impurities.—Heavy metals, calcium, chloride, sulphate.

Sodium Peroxide, Na_2O_2=78·0. (Na_2O, 79·49; O, 20·51.)—Decomposed by water into sodium hydroxide and hydrogen peroxide.

Determination.—Place 0·5 gm. of the salt in a Schrötter apparatus or in an ordinary flask. In the upper limb of the Schrötter apparatus or in a short test-tube placed inside the flask put 15 cc. of dilute sulphuric acid containing 2 or 3 drops of cobalt nitrate solution. The solution is later brought in contact with the peroxide and oxygen is evolved, which, from the flask, may be measured in a nitrometer in the usual way, or, in the Schrötter apparatus may be determined by the loss in weight of the flask. The commercial salt usually contains about 93 per cent. of pure Na_2O_2.

Common Impurities.—Heavy metals, calcium, chloride, sulphate, phosphate, nitrate, silica.

Sodium Phenate (Sodium carbolate), C_6H_5ONa=116·1. (Na, 19·82; C_6H_5OH, 81·05.)—A white, deliquescent powder, readily soluble in water.

Determination of Sodium.—May be determined as given under Potassium Citrate. 1 cc. $N/2$ HCl ≡ 0·05804 gm. C_6H_5ONa.

Phenol.—Dissolve 1 gm. in 100 cc. of water. Pipette 5 cc. into a mixture of 50 cc. of water, 5 cc. of hydrochloric acid, and 50 cc. of $N/10$ bromide-bromate solution. Shake during fifteen minutes, add 2 gm. of potassium iodide dissolved in 5 cc. of water and titrate with $N/10$ thiosulphate. 1 cc. $N/10$ Br ≡ 0·001935 gm. C_6H_5ONa or 0·001568 gm. C_6H_5OH.

Arsenic.—Char 2 gm. in a porcelain dish, dissolve in 14 cc. of brominated hydrochloric acid and 50 cc. of water, remove excess of bromine with stannous chloride solution and proceed as usual. Limit, 5 parts per million.

Lead.—No appreciable darkening should take place on adding sodium sulphide solution to a 5 per cent. solution of the salt.

Sodium Phenolsulphonate (Sodium sulphocarbolate), $NaC_6H_5O.SO_3.2H_2O$=232·2. (Na, 9·92; $C_6H_5O.SO_3$, 74·57; H_2O, 15·51.)—White, odourless prisms. Solubility in water, 13; in alcohol, 0·7; in glycerin, 20. The water of crystallisation is completely lost at 100° C.

Determination.—Dissolve 0·2 gm. in 50 cc. of water, add 50 cc. of $N/10$ bromide-bromate mixture and 5 cc. of hydrochloric acid. Shake during fifteen minutes, then add 2 gm. of potassium iodide dissolved in 5 cc. of water and titrate with $N/10$ sodium thiosulphate. 1 cc. $Na_2S_2O_3$ ≡ 0·005804 gm. $NaC_6H_5O.SO_3.2H_2O$, or 0·004903 gm. $NaC_6H_5O.SO_3$. The U.S.P. requires 83·6 to 87·4 per cent. of $C_6H_5OSO_3Na$.

Tests.—The aqueous solution should be neutral and should not yield a precipitate with ferric chloride (a violet colour is produced). Chlorides and free phenol should be absent, the latter being shown by the aqueous solution giving no precipitate with bromine water.

Arsenic.—Char 2 gm. in a porcelain dish, dissolve the residue in 14 cc. of brominated hydrochloric acid, remove excess of bromine with a few drops of stannous chloride solution and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 10 parts per million.

Sodium Phosphate (Disodium hydrogen phosphate), $Na_2HPO_4.12H_2O$= 358·2. (Na, 12·84; PO_4, 26·53; H_2O, 60·35.)—Solubility in water, 13; insoluble in alcohol.

Determination of Alkalinity.—Dissolve 5 gm. in water, add 25 cc. of $N/2$ hydrochloric acid and continue the titration with the same acid to methyl red until the maximum red colour is reached. 1 cc. $N/2$ HCl ≡ 0·1791 gm. $Na_2HPO_4.12H_2O$ or 0·07104 gm. Na_2HPO_4.

Phosphate.—Dissolve 1 gm. in 100 cc. of water, add ammonia until the liquid smells slightly ammoniacal; then add 20 cc. of magnesia mixture drop by drop with continuous shaking. Allow the mixture to stand fifteen minutes and add 25 cc. of 10 per cent. ammonia. Allow to stand at least twelve hours. Filter, wash with 3 per cent. ammonia, and ignite to magnesium pyrophosphate. $Mg_2P_2O_7 \times 1{\cdot}276 = Na_2HPO_4$ or $Mg_2P_2O_7 \times 3{\cdot}217 = Na_2HPO_4.12H_2O$. The B.P. requires the salt to contain not less than 99·5 per cent. $Na_2HPO_4.12H_2O$. The U.S.P. salt contains not less than 39·25 or more than 44·0 per cent. of Na_2HPO_4. When the phosphate is not pure it should be first precipitated with molybdic acid solution, the precipitate washed, dissolved in 3 per cent. ammonia, the solution made nearly neutral, and then precipitated with magnesia mixture as described above. The anhydrous salt is official in the U.S.P.; it is prepared by drying the crystals at 110° C. It is required to contain not less than 98 per cent. of Na_2HPO_4.

Common Impurities.—Ammonium, calcium, aluminium, carbonate, sulphate, and chloride.

Arsenic.—By the general method on 7 gm. with 2 gm. in the control. Limit, 5 parts per million.

Sodium (Acid) Phosphate, $NaH_2PO_4.2H_2O = 156{\cdot}1$. (Na, 15·38; PO_4, 60·86; H_2O, 23·08.)—Solubility in water, 84; insoluble in alcohol. The aqueous solution is acid to litmus. The whole of the water of crystallisation, which is somewhat variable in amount, is lost from the salt at 100° C.

Determination of Alkalinity.—Dissolve 2 gm. in 20 cc. of water, add 20 cc. of glycerin, and titrate with *N*/2 sodium hydroxide to phenolphthalein or thymol blue to a blue colour ($pH = 9{\cdot}1$). 1 cc. *N*/2 NaOH ≡ 0·06003 gm. NaH_2PO_4 or 0·07804 gm. $NaH_2PO_4.2H_2O$. The B.P. requires not less than 70 per cent. NaH_2PO_4 when determined by titration with sodium hydroxide.

Phosphate.—On 1 gm., as given under Sodium Phosphate. $Mg_2P_2O_7 \times 1{\cdot}402 = NaH_2PO_4.2H_2O$, or $Mg_2P_2O_7 \times 1{\cdot}088 = NaH_2PO_4$.

Common Impurities.—Ammonium, calcium, aluminium, carbonate, sulphate, and chloride.

Arsenic.—By the general method on 5 gm. Limit, 5 parts per million. (B.P., 2 parts per million).

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 5 parts per million.

Sodium Potassium Tartrate (Rochelle Salt), $NaKC_4H_4O_6.4H_2O = 282{\cdot}2$. (Na, 8·15; K, 13·86; $C_4H_4O_6$, 52·46; H_2O, 25·53.)—Solubility in water, 53 (anhydrous salt); insoluble in alcohol or ether. The aqueous solution should be neutral to phenolphthalein and to litmus.

Determination.—On 2·5 gm. by the method given under Potassium Citrate. 1 cc. *N*/2 HCl ≡ 0·07055 gm. $NaKC_4H_4O_6.4H_2O$, or 0·05254 gm. $NaKC_4H_4O_6$. The B.P. requires not less than 98 per cent. of $NaKC_4H_4O_6.4H_2O$.

Common Impurities.—Copper, iron, calcium, ammonia, chloride, and sulphate.

Arsenic.—By the general method on 5 gm., using 14 cc. of stannated hydrochloric acid. Limit, 2 parts per million.

Lead.—By the general method on 3 gm. with 1 gm. in the control. Limit, 20 parts per million.

Sodium Salicylate, $C_6H_4.OH.COONa$=160·1. (Na, 14·37; $C_6H_4.OH.COOH$, 86·25.)—Consists of white, pearly scales or a white powder. Solubility in water, 110; in alcohol, 5; soluble also in glycerin.

Determination of Sodium.—By the method given under Potassium Citrate or under Ammonium Benzoate. 1 cc. *N*/2 HCl ≡ 0·08004 gm. $C_6H_4.OH.COONa$.

Salicylic Acid.—By the method given under Ammonium Benzoate, $C_6H_4OH.COOH \times 1{\cdot}1585 = C_6H_4OH.COONa$.

Free Salicylic Acid.—Dissolve 2 gm. in water and titrate with *N*/10 sodium hydroxide to phenolphthalein or thymol blue. 1 cc. *N*/10 NaOH ≡ 0·01381 gm. $C_6H_4OH.COOH$.

Tests.—The B.P. requires that the salt shall not evolve the slightest odour of phenol when 50 to 100 gm. are kept in a closed bottle for several days, and that it shall dissolve without coloration or effervescence in conc. sulphuric acid.

Arsenic.—Char 5 gm. in a porcelain dish. Dissolve the residue in 16 cc. of brominated hydrochloric acid and 50 cc. of water, remove the excess of bromine with a few drops of stannous chloride solution and proceed as usual. Limit, 2 parts per million. In the electrolytic process the general method may be used.

Lead.—Dissolve 2 gm. in 50 cc. of water and add a few drops of sodium sulphide solution; no appreciable darkening should take place.

Sodium Sulphate (Glauber's Salts), $Na_2SO_4.10H_2O$=322·2. (Na, 14·28; SO_4, 29·81; H_2O, 55·91.)—A white powder or crystals which should not obviously be effloresced. The whole of the water of crystallisation is lost at 100° C. Solubility in water, 36; insoluble in alcohol.

Determination of Sodium.—Heat 2 gm. with 2 cc. of conc. sulphuric acid until white fumes cease to be evolved, then ignite until constant in weight. $Na_2SO_4 \times 2{\cdot}2682 = Na_2SO_4.10H_2O$.

Sulphate.—Dissolve 0·5 gm. in 300 cc. of water in a 600-cc. beaker and heat. When the solution is boiling pour in drop by drop a boiling solution of 2 gm. of barium chloride solution in 20 cc. of water and continue the boiling for a few minutes. Allow to stand twelve hours. Filter, wash by decantation, ignite, and weigh as $BaSO_4$. $BaSO_4 \times 1{\cdot}381 = Na_2SO_4.10H_2O$.

Common Impurities.—Iron, calcium, ammonium, chloride, nitrate, and nitrite.

Arsenic.—By the general method on 5 gm. Limit, 2 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 5 parts per million.

Sodium Sulphate, Anhydrous, Na_2SO_4=142·1.—A white powder. Solubility in water, 13.

Moisture.—The loss at 100° C. should not be more than 1 per cent. In other respects this salt should conform to the tests for hydrated sodium sulphate. $BaSO_4 \times 0{\cdot}6088 = Na_2SO_4$.

Sodium Sulphide, $Na_2S.9H_2O$=240·2. (Na, 19·15; S, 13·35; H_2O, 67·50.)—Solubility in water, 100.

Determination.—Dissolve 1 gm. in water and dilute to 100 cc. Take 20 cc. of this solution and add 20 cc. of *N*/10 iodine, 100 cc. of water, and 3 cc. of conc. hydrochloric acid. Shake well and titrate the residual iodine with *N*/10 sodium thiosulphate. 1 cc. *N*/10 I ≡ 0·01201 gm. $Na_2S.9H_2O$ or 0·003903 gm. Na_2S.

Tests.—5 gm. should dissolve in water to form a clear solution, whilst 1 gm. in 20 cc. of water with 2 cc. of hydrochloric acid should evolve sulphuretted hydrogen and form a solution which is only faintly opalescent.

Sodium Sulphite, $Na_2SO_3.7H_2O$=252·2. (Na, 18·24; SO_3, 31·75; H_2O, 50·01.)—Solubility in water, 100; insoluble in alcohol. It loses the whole of its water of crystallisation at 100° C.

Determination.—Dissolve 0·972 gm. in 100 cc. of air-free water and with this titrate 20 cc. of *N*/10 iodine acidified with hydrochloric acid. The percentage of $Na_2SO_3.7H_2O = \frac{10,000}{4 \times \text{No. of cc. used}}$. 1 cc. *N*/10 I ≡ 0·01261 gm. $Na_2SO_3.7H_2O$ or 0·006303 gm. Na_2SO_3.

Tests.—The aqueous solution should be clear and bright, and, on the addition of hydrochloric acid, sulphur dioxide should be evolved, but no cloudiness should be produced in the solution.

Arsenic.—Mix 2 gm. with 0·5 gm. of potassium chlorate and dissolve in 5 cc. of water; add 12 cc. of hydrochloric acid and allow to stand one hour. Warm to expel excess of chlorine, add 50 cc. of water, a few drops of stannous chloride solution, and proceed as usual. Limit, 5 parts per million. In the electrolytic process the method for Hypophosphites should be used.

Lead.—2 gm. by general method.

Sodium Tartrate, $Na_2C_4H_4O_6.2H_2O$=230·1. (Na, 19·99; $C_4H_4O_6$, 64·32; H_2O, 15·69.)—Solubility in water, 40; insoluble in alcohol.

Determination.—On 2 gm. by the method given under Potassium Citrate. 1 cc. *N*/2 HCl ≡ 0·05752 gm. $Na_2C_4H_4O_6.2H_2O$ or 0·04851 gm. $Na_2C_4H_4O_6$.

Common Impurities.—Copper, iron, calcium, potassium, ammonia, chloride, sulphate.

Arsenic.—Char 2 gm. in a porcelain dish, treat the residue with 14 cc. of brominated hydrochloric acid and 50 cc. of water, remove the excess of bromine with a few drops of stannous chloride solution and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—By the general method on 4 gm. with 2 gm. in the control. Limit, 20 parts per million.

Sodium Tauroglycocholate.—This is the sodium salt of a mixture of acids occurring in ox bile; it consists chiefly of sodium taurocholate and sodium glycocholate. It is a yellow-brown, amorphous, hygroscopic powder with a sour, irritating smell, completely soluble in water and alcohol. It is chiefly used in the preparation of bacteriological media.

Tests.—Dissolve a small quantity in water, add two-thirds of its volume of conc. sulphuric acid drop by drop and then a few drops of syrup; an intense violet or purple-red colour is produced. On boiling with sodium hydroxide under a reflux condenser for several hours a solution is obtained which, on acidifying with hydrochloric acid, gives a stringy, yellowish mass of cholic acid.

Sodium Thiosulphate (Sodium "Hyposulphite"), $Na_2S_2O_3.5H_2O$=248·2. (Na, 18·53; S_2O_3, 45·18; H_2O, 36·29.)—Solubility in water, 65; insoluble in alcohol. The *p*H value of a 2 per cent. solution should lie between 6 and 9.

Determination.—Dissolve 1 gm. in 20 cc. of water, add 50 cc. of *N*/10 iodine and titrate back with *N*/10 sodium thiosulphate. 1 cc. *N*/10 I ≡ 0·02482 gm. $Na_2S_2O_3.5H_2O$. The crystallised salt should contain not

less than 99 per cent. $Na_2S_2O_3.5H_2O$; the commercial salt not less than 97 per cent.

Calcium.—Dissolve 1 gm. in 20 cc. of water and add ammonium oxalate solution; no immediate turbidity should be produced.

Sulphur Compounds.—Dissolve 1 gm. in 20 cc. of water and add a few drops of silver nitrate solution; a pure white precipitate free from any suggestion of brown should be produced.

Sulphite and Sulphate.—The solution obtained from the titration above should not give more than a slight turbidity with barium chloride.

Sodium Tungstate, $Na_2WO_4.2H_2O$=330·0. (Na, 13·93; WO_3, 70·33; H_2O, 10·92.)—Solubility in water, 80.

Determination.—Dissolve 1 gm. in 10 cc. of water, add 10 cc. of conc. hydrochloric acid, evaporate to dryness and heat for an hour at 120° C. Moisten with hydrochloric acid, dilute with water, boil, filter, wash with hydrochloric acid (S.G. 1·03), ignite and weigh as WO_3. $WO_3 \times 1{\cdot}422 = Na_2WO_4.2H_2O$. Not less than 98 per cent. should be indicated.

Impurities.—Chloride, sulphate, and nitrate.

Sodium Valerate (Sodium Valerianate), $C_5H_9O_2Na$=124·1. (Na, 18·54; $C_5H_9O_2H$, 82·27.)—Readily soluble in water or alcohol.

Determination.—On 1 gm., as given under Potassium Citrate. 1 cc. $N/2$ HCl ≡ 0·06204 gm. $NaC_5H_9O_2$.

Free Valeric Acid.—Dissolve 2 gm. in water and titrate with $N/10$ hydrochloric acid to phenolphthalein. 1 cc. $N/10$ HCl ≡ 0·0102 gm. $HC_5H_9O_2$.

Arsenic.—Char 2 gm. in a porcelain basin, dissolve in 14 cc. of brominated hydrochloric acid and 50 cc. of water, remove excess of bromine with a few drops of stannous chloride solution and proceed as usual. Limit, 5 parts per million. In the electrolytic process the method for Halogen Salts should be used.

Lead.—By the general method on 4 gm. with 2 gm. in the control. Limit, 10 parts per million.

Stannous Chloride, $SnCl_2.2H_2O$=225·6. (Sn, 52·60; Cl, 31·43; H_2O, 15·97.)—Readily soluble in water, alcohol or ether; the aqueous solution precipitates a basic compound on dilution.

Determination.—Dissolve 0·5 gm. in 2 cc. of conc. hydrochloric acid, dilute the solution to 50 cc. with water, add 5 gm. of Rochelle salt and sodium bicarbonate until the solution is alkaline to litmus paper. Titrate with $N/10$ iodine solution, using starch as an indicator. 1 cc. $N/10$ I ≡ 0·01128 gm. $SnCl_2.2H_2O$.

Impurities.—Dissolve 2 gm. in 6 cc. of conc. hydrochloric acid, dilute to 100 cc., completely precipitate the tin with sulphuretted hydrogen, evaporate the filtrate to dryness and ignite. The residue should not exceed 1 mg. An immediate precipitate should not be given when barium chloride is added to a solution of 1 gm. of the salt in dilute hydrochloric acid.

Arsenic.—Mix 1 gm. with 16 cc. of water and 10 cc. of hydrochloric acid and distil 16 cc. Dilute the distillate with water, add a few drops of stannous chloride solution and proceed as usual. Limit, 20 parts per million.

Strontium Bromide, $SrBr_2.6H_2O$=355·6. (Sr, 24·65; Br, 44·95; H_2O, 30·40.)—Solubility in water, 230; soluble in alcohol; insoluble in ether.

Determination of Strontium.—Treat 1 gm. with 2 or 3 cc. of conc. sulphuric acid; heat gently until white fumes cease to be evolved and then ignite until constant in weight. $SrSO_4 \times 1{\cdot}9357 = SrBr_2.6H_2O$; $SrSO_4 \times 1{\cdot}3472 = SrBr_2$.

Bromide.—Dissolve 0·7 gm. in 50 cc. of water, add 50 cc. of $N/10$ silver nitrate and titrate back with $N/10$ thiocyanate. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·01237 gm. $SrBr_2$ or 0·01778 gm. $SrBr_2.6H_2O$. The B.P. requires not less than 67·5 per cent. of $SrBr_2$.

Separation of Strontium from Barium and Calcium.—The best method is to prepare the mixed nitrates by repeated evaporation with nitric acid, extract these with ethereal alcohol to remove the calcium nitrate and separate the barium and strontium by the chromate process given below. The separated products are converted into sulphates and weighed.

Separation of Strontium and Barium.—About 1 gm. of the salt is dissolved in acetic acid and slight excess of potassium chromate added. The precipitated barium chromate is filtered off, dissolved in the smallest amount of hydrochloric acid, the solution treated with sodium acetate and acetic acid and the barium again precipitated as chromate and filtered. The two filtrates are mixed, the strontium is precipitated as carbonate, converted into sulphate and weighed.

Tests.—A saturated solution of calcium sulphate should give a white precipitate with a 10 per cent. solution of the salt. 1 gm. dissolved in water, with the addition of 5 cc. of a 10 per cent. solution of sodium acetate and 3 cc. of acetic acid (S.G. 1·07), should not give a precipitate on the addition of potassium chromate solution, showing absence of barium.

Strontium Iodide, $SrI_2.6H_2O = 449{\cdot}6$. (Sr, 19·49; I, 56·47; H_2O, 24·04.)—Solubility in water, 500; soluble in alcohol; slightly soluble in ether.

Determination of Strontium.—As under Strontium Bromide. $SrSO_4 \times 2{\cdot}448 = SrI_2.6H_2O$; $SrSO_4 \times 1{\cdot}859 = SrI_2$.

Iodide.—Dissolve 1 gm. in 25 cc. of water, add 50 cc. of $N/10$ silver nitrate, and titrate back with $N/10$ thiocyanate. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·02248 gm. $SrI_2.6H_2O$ or 0·01707 gm. SrI_2.

Tests.—For separation from calcium and barium see under Strontium Bromide above.

Strontium Lactate, $Sr(C_3H_5O_3)_2.3H_2O = 319{\cdot}8$. (Sr, 27·41; $C_3H_5O_3$, 55·69; H_2O, 16·90.)—Solubility in water, 20.

Determination.—Treat 1 gm. in a crucible with conc. sulphuric acid, carefully ignite, cool, and repeat the process; finally ignite until constant in weight. $SrSO_4 \times 1{\cdot}741 = Sr(C_3H_5O_3)_2.3H_2O$; $SrSO_4 \times 1{\cdot}446 = Sr(C_3H_5O_3)_2$.

Tests.—For methods of separation from barium and calcium see Strontium Bromide.

Arsenic.—Ignite 2 gm. in a porcelain dish, treat with 14 cc. of brominated hydrochloric acid and 50 cc. of water, remove excess of bromine with a few drops of stannous chloride solution and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Lead.—2 gm. dissolved in 50 cc. of water should show no appreciable darkening on the addition of 3 drops of sodium sulphide solution.

Strontium Nitrate, $Sr(NO_3)_2 = 211{\cdot}65$. (SrO, 48·96; NO_3, 58·60.)—Solubility in water, 60; very slightly soluble in alcohol.

Determination.—Ignite 2 gm. at first carefully and then strongly until

constant in weight. $SrO \times 2{\cdot}0429 = Sr(NO_3)_2$. The purity of the strontium oxide produced may be checked by heating with sulphuric acid and igniting until constant in weight. $SrSO_4 \times 0{\cdot}5641 = SrO$; $SrSO_4 \times 1{\cdot}1521 = Sr(NO_3)_2$.

Tests.—For separation from calcium and barium and tests for purity see under Strontium Bromide above.

Sulphur, S=32·06.

Precipitated Sulphur.—A pale greenish-yellow, fine powder, free from grittiness. Insoluble in water; slightly soluble in alcohol; readily soluble in carbon disulphide, chloroform, and olive oil.

Determination.—As given under Sublimed Sulphur.

Microscopic Examination.—No crystals should be apparent.

B.P. Tests.—Ash, less than 0·5 per cent. If 10 gm. are shaken with water, filtered and washed, the filtrate should not require more than 2 cc. of *N*/10 sodium hydroxide when neutralised to phenolphthalein.

Arsenic.—Digest 2 gm. on the water bath with 50 cc. of water and 5 cc. of ammonium hydroxide (S.G. 0·96) for one hour; filter, evaporate the filtrate to low bulk, add 10 cc. of nitric acid, and boil to oxidise the sulphur. Add 2 cc. of sulphuric acid, heat until white fumes are evolved, add 50 cc. of water, 10 cc. of stannated hydrochloric acid, and proceed as usual. Limit, 5 parts per million. In the electrolytic process the general method may be used.

Sublimed Sulphur ("Flowers" of Sulphur).—The latter term is sometimes wrongly applied to ground sulphur not prepared by sublimation. The latter product is entirely soluble in carbon disulphide. Sublimed sulphur occurs as a bright yellow, fine powder, free from grittiness. Under the microscope it consists largely of amorphous particles. Its solubility is similar to that of precipitated sulphur above, except that a portion is insoluble in carbon disulphide.

Determination.—Boil 1 gm. of sulphur with 50 cc. of 10 per cent. potassium hydroxide until the liquid is clear, and dilute to 250 cc. Oxidise 25 cc. of this solution by heating on the water bath for half an hour with 50 cc. of 3 per cent. hydrogen peroxide solution, acidify with hydrochloric acid, and dilute to 100 cc. Determine the sulphate as barium sulphate in the usual way. $S = BaSO_4 \times 0{\cdot}1373$.

Ash.—Not more than 0·25 per cent., B.P.

Acidity.—Shake 0·5 gm. with 10 cc. of neutral distilled water for about five minutes. Filter and test the filtrate with 3 drops of thymol blue. A pure yellow colour should be obtained without a trace of orange or pink.

Arsenic.—On 2 gm. as under Precipitated Sulphur. Limit, 5 parts per million.

Total Solids and Ash.—Determine the total solids in 10 cc. as usual. Ignite the solids and determine the ash.

Arsenic.—On 10 cc. as given under Precipitated Sulphur. Limit, 5 parts per million.

Sulphur Iodide.—Occurs as a greyish-black, crystalline solid, with an odour resembling that of iodine. The iodine is evolved on boiling the substance with water. Insoluble in water; solubility in carbon disulphide, 25; in glycerin, 1·6.

Determination.—Dissolve 0·5 gm. in 20 cc. of potassium iodide solution, and titrate with *N*/10 thiosulphate. 1 cc. *N*/10 $Na_2S_2O_3 \equiv 0{\cdot}01269$ gm. I.

The sulphur remains undissolved during the titration. The U.S.P. requires not less than 71 per cent. of iodine.

Sulphuric Acid, H_2SO_4=98·1. (H, 2·06; SO_4, 97·94.)—The purest sulphuric acid of commerce contains about 98 per cent. of hydrogen sulphate, the remainder being water.

Determination.—Weigh 1 gm. in a weighing bottle, dilute with water, and titrate with *N*/2 sodium hydroxide solution to methyl red. (1 cc. *N*/2 NaOH ≡ 0·02452 gm. H_2SO_4.) The strength may also be checked from the specific gravity, using the table due to Lunge and Isler (see Appendix) or by precipitating as barium sulphate as given under Sodium Sulphate. $BaSO_4 \times 0·4202 = H_2SO_4$.

B.P. Strengths.—The sulphuric acid official in the B.P. has S.G. about 1·841, and contains not less than 95 per cent. of pure acid; the diluted sulphuric acid has S.G. 1·069 and contains 10 per cent. of pure acid, whilst aromatic sulphuric acid (*Acidum Sulphuricum Aromaticum*, B.P.) has S.G. 0·917 to 0·923, and 10 cc. should require not less than 49·8 cc. of *N*/2 sodium hydroxide.

Solid Impurities.—10 gm. should not leave any weighable residue on evaporation and ignition. (Not more than 0·05 per cent., B.P.).

Common Impurities.—Copper, iron, nitrogen compounds, chloride, and sulphite.

Permanganate Test.—Dilute 15 cc. of acid with 60 cc. of water, cool, and add 1 drop of *N*/10 potassium permanganate; the solution should remain red for five minutes.

Nitric Acid.—10 cc. are added to a mixture of 10 cc. of water and 0·5 cc. of indigo solution; the mixture should remain blue.

Nitrogen Compounds.—Treat 20 cc. of the acid with 1 gm. of pure cane sugar by Kjeldahl's process; not more than 0·3 cc. of *N*/10 hydrochloric acid should be required.

Selenium.—Add 3 cc. of hydrochloric acid containing a little sodium sulphite to 3 cc. of the sulphuric acid, so that a layer is formed; no red colour or precipitate should appear on warming.

Arsenic.—On 2 gm. by the general method, using 8 cc. of hydrochloric acid. Limit, 5 parts per million. The acid sold as "Arsenic-free" should contain less than 0·1 part per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 20 parts per million.

Sulphurous Acid, H_2SO_3=82·1.—A colourless, pungent smelling solution containing (according to the B.P.) 6·4 per cent. of sulphurous acid, which is equivalent to 5 per cent. by weight of sulphur dioxide. S.G. 1·025.

Determination.—Dilute 10 gm. to 100 cc. with recently boiled and cooled distilled water, and run 10 cc. of the diluted solution from a pipette *slowly* into 25 cc. of *N*/10 iodine; titrate the excess of iodine with *N*/10 thiosulphate. 1 cc. *N*/10 I ≡ 0·003203 gm. SO_2, or 0·004104 gm. H_2SO_3.

It should only give a slight reaction for *sulphate.*

Arsenic.—Mix 2 gm. with 0·5 gm. of potassium chlorate and 10 cc. of hydrochloric acid in the cold; warm to expel excess of chlorine, add 50 cc. of water and a few drops of stannous chloride solution, and proceed as usual. Limit, 5 parts per million. (For the electrolytic method, see p. 31.)

Lead.—By the general method on 12 gm. with 2 gm. in the control. Limit, 10 parts per million.

Talc (French Chalk).—Talc is a native hydrated magnesium silicate usually containing some aluminium silicate. It is purified by boiling with hydrochloric acid. Purified talc is a fine white powder, which has a greasy feel when rubbed on the skin. It should be free from grittiness. On heating to redness, talc should not lose more than 5 per cent. When 1 gm. of purified talc is boiled under a reflux condenser with 25 cc. of dilute hydrochloric acid for thirty minutes, the filtrate, on evaporation and ignition, should yield not more than 50 mg. of residue.

Uranium Acetate, $UO_2(CH_3.COO)_2.3H_2O=442·3$. ($CH_3.COOH$, 27·14; UO_2, 61·09; H_2O, 12·23.)—Soluble in water and alcohol.

Determination.—Dissolve 0·2 gm. in 50 cc. of water, boil, and add ammonia until no further precipitate is produced. Filter, wash with 1 per cent. ammonium nitrate solution, ignite to constant weight, and weigh as U_3O_8. $U_3O_8 \times 1·5748=UO_2(CH_3.COO)_2.3H_2O$; $U_3O_8 \times 1·3823=UO_2.(CH_3.COO)_2$.

Impurities.—Dissolve 1 gm. in 25 cc. of water and completely precipitate by boiling with excess of ammonia; filter, evaporate the filtrate to dryness and ignite; the residue should not exceed 4 mgm.

Tests.—A 5 per cent. solution should give no colour with an equal volume of sulphuretted hydrogen water. Barium chloride should give no precipitate.

Uranium Nitrate, $UO_2(NO_3)_2.6H_2O=502·3$. (UO_2, 53·79; NO_3. 24·69; H_2O, 21·52.) Solubility in water, 200; in alcohol (85 per cent.), 3·3; soluble in ether.

Determination.—As under Uranium Acetate. $U_3O_8 \times 1·788 = UO_2(NO_3)_2.6H_2O$; $U_3O_8 \times 1·4036=UO_2(NO_3)_2$.

Impurities and Tests.—As given under Uranium Acetate above.

Zinc, $Zn=65·37$.

Determination of Arsenic.—For the purpose of testing for arsenic, zinc should be granulated in not too large pieces, and should comply with the following test: 10 cc. of stannated hydrochloric acid are added to 50 cc. of warm water and 10 gm. of the zinc. The test is carried out in the usual way for arsenic. Not more than the faintest stain should be obtained. The same test should be carried out with the addition of 1 cc., 0·5 cc., and 0·2 cc. of the standard solution of arsenic. The stains produced should be of proportionate depth and easily distinguishable.

Iron.—Dissolve 20 gm. in a slight excess of hydrochloric acid, boil with a few drops of nitric acid, add excess of ammonia, filter, and wash with water. Only a slight brown precipitate of ferric hydroxide should remain.

Zinc Acetate, $Zn(C_2H_3O_2)_2.2H_2O=219·5$. (Zn, 29·79; $C_2H_3O_2$, 53·79; H_2O, 16·42.)—Solubility in water, 40; in alcohol, 3.

Determination.—Dissolve 1 gm. in 100 cc. of water, make slightly alkaline with ammonia, and heat to 80° C. Add ammonium sulphide until the whole of the zinc is precipitated, and warm on the water bath until the precipitate settles. Filter, wash with water containing a few drops of ammonium sulphide, dissolve in hot dilute nitric acid, evaporate to dryness, ignite, and weigh as ZnO. $ZnO \times 2·6972=Zn(C_2H_3O_2)_2.2H_2O$; $ZnO \times 2·2544= Zn(C_2H_3O_2)_2$.

Common Impurities.—Lead, copper, cadmium, iron, chloride, and sulphate.

Alkali Metals.—The filtrate from the above determination evaporated to dryness and ignited should not yield more than 1 mg. of residue.

Manganese.—Dissolve 0·5 gm. in water, add excess of ammonia, and allow to stand. Filter off any precipitate formed, dissolve this in dilute nitric acid, dilute to about 15 cc. with water, heat to boiling, and add 1 cc. of *N*/10 silver nitrate solution and 10 cc. of a 10 per cent. solution of ammonium persulphate. The solution should not acquire more than the faintest pink tinge.

Other Metals.—The precipitate with ammonia and sodium sulphide should not be deeper than very pale brown.

Arsenic.—On 2 gm. by the general method. Limit, 10 parts per million.

Zinc Benzoate, $(C_6H_5COO)_2.Zn$=307·4. (Zn, 21·27; C_6H_5COOH, 79·47.)—Slightly soluble in water.

Determination of Benzoic Acid.—Dissolve 2 gm. in 50 cc. of hot water acidified with dilute sulphuric acid. Cool, extract with three portions each of 20 cc. of ether, and wash the ethereal solution with two portions of 5 cc. of water. Shake with 50 cc. of *N*/2 sodium hydroxide, and titrate back with *N*/2 hydrochloric acid to phenolphthalein. 1 cc. *N*/2 NaOH ≡ 0·06104 gm. C_6H_5COOH, or 0·0769 gm. $(C_6H_5COO)_2Zn$. Alternatively, the ethereal solution may be evaporated to dryness at a low temperature, the benzoic acid dried in a desiccator and weighed.

Zinc.—Take the mixed aqueous washings from the determination of benzoic acid above, and determine the zinc as given under Zinc Acetate. ZnO×0·8034=Zn; ZnO×3·7784=$(C_6H_5COO)_2.Zn$.

Impurities.—These may be tested for as under Zinc Acetate.

Arsenic.—Make 2 gm. into a paste with 2 gm. of calcium hydroxide and 5 cc. of water; dry and ignite gently. Treat the residue with 18 cc. of brominated hydrochloric acid and 40 cc. of water, remove excess of bromine with a few drops of stannous chloride solution, and proceed as usual. Limit, 10 parts per million. In the electrolytic process the general method may be used.

Zinc Bromide, $ZnBr_2$=225·2. (Zn, 29·02; Br, 70·98.)—Solubility in water, 400; in alcohol, 200; soluble in ether.

Determination.—Dissolve 0·4 gm. in 20 cc. of water, add 50 cc. of *N*/10 $AgNO_3$, 2 cc. of dilute nitric acid, and titrate back with *N*/10 thiocyanate. 1 cc. *N*/10 $AgNO_3$ ≡ 0·01126 gm. $ZnBr_2$.

Impurities.—As under Zinc Acetate.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million. In the electrolytic process the method for Halogen Salts (p. 33) must be used.

Other Metals.—The precipitate formed by treating 0·5 gm. dissolved in 50 cc. of water with ammonia and sodium sulphide solution should not be deeper in colour than pale brown.

Zinc Carbonate.—A basic carbonate of zinc of somewhat variable composition. The B.P. gives the formula, $ZnCO_3.[Zn(OH)_2]_2.H_2O$=342·2. Insoluble in water.

Determination.—Dissolve 1 gm. in 50 cc. of *N*/2 sulphuric acid, boil, cool, and titrate back with *N*/2 sodium hydroxide to bromophenol blue. 1 cc. *N*/2 H_2SO_4 ≡ 0·02034 gm. ZnO. The U.S.P. requires not less than 88 per cent. of ZnO.

Impurities.—As under Zinc Acetate.

Arsenic.—On 2 gm. by the general method, using 18 cc. of brominated hydrochloric acid, and removing excess of bromine with stannous chloride solution. Limit, 10 parts per million. In the electrolytic process the general method may be used.

Other Metals.—Dissolve 1 gm. in dilute hydrochloric acid, boil, make alkaline with ammonia, and precipitate with sodium sulphide; the precipitate should not be deeper than pale brown in colour.

Zinc Chloride, $ZnCl_2$=136·3. (Zn, 47·96; Cl, 52·04.)—Solubility in water, 340; in alcohol, 100; soluble in ether and glycerin.

Determination of Zinc.—As under Zinc Acetate. $ZnO \times 1{\cdot}6749 = ZnCl_2$; $ZnO \times 0{\cdot}8034 = Zn$.

Chloride.—Weigh 0·3 gm. in a weighing bottle, and titrate with N/10 silver nitrate, using potassium chromate as indicator. 1 cc. N/10 $AgNO_3 \equiv$ 0·006815 gm. $ZnCl_2$.

Impurities.—As under Zinc Acetate.

Arsenic.—By the general method on 2 gm. Limit, 10 parts per million. In the electrolytic process use the method for Halogen Salts (p. 33).

Other Metals.—As under Zinc Acetate.

Zinc Iodide, ZnI_2=319·2. (Zn, 20·48; I, 79·52.)—Readily soluble in water, 400; also soluble in alcohol and ether.

Determination of Zinc.—As under Zinc Acetate. $ZnO \times 3{\cdot}923 = ZnI_2$; $ZnO \times 0{\cdot}8034 = Zn$.

Iodide.—Dissolve 0·6 gm. in water, add 50 cc. of N/10 silver nitrate, and titrate back with N/10 thiocyanate. 1 cc. N/10 $AgNO_3 \equiv$ 0·01596 gm. ZnI_2.

Impurities.—As under Zinc Acetate.

Arsenic.—By the general method on 2 gm. Limit, 10 parts per million. In the electrolytic process use the method for Halogen Salts (p. 33).

Other Metals.—As under Zinc Acetate.

Zinc Oleostearate.—A white, amorphous powder obtained by precipitating a solution of a mixture of hard and curd soaps with a solution of zinc sulphate. Insoluble in water, alcohol, and ether.

Tests.—As under Zinc Stearate.

Zinc Oxide, ZnO=81·4. (Zn, 80·34; O, 19·66.)—Insoluble in water, soluble in dilute acids to a clear solution with no black particles.

Determination of Zinc.—As under Zinc Acetate after solution in dilute hydrochloric acid. $ZnO \times 0{\cdot}8034 = Zn$.

Oxide.—Treat 1·5 gm. with 50 cc. of N sulphuric acid until complete solution has taken place; titrate back with N/2 NaOH to bromophenol blue. 1 cc. N $H_2SO_4 \equiv$ 0·04069 gm. ZnO.

Impurities.—As under Zinc Acetate. Carbonates and nitrates should not be present.

Arsenic.—As under Zinc Carbonate. Limit, 10 parts per million.

Other Metals.—As under Zinc Acetate after solution in hydrochloric acid.

Zinc Permanganate, $Zn(MnO_4)_2.6H_2O$=411·3. (Zn, 15·89; MnO_4, 57·83; H_2O, 26·28.)—Forms dark brownish-violet crystals resembling those of potassium permanganate. Solubility in water, 25, leaving not more than a trace of residue.

Determination.—Dissolve 1 gm. in water; dilute to 100 cc. Take 10 cc. of this solution, add 10 cc. of potassium iodide solution and 5 cc. of dilute

hydrochloric acid, and titrate the liberated iodine with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}004113$ gm. $Zn(MnO_4)_2.6H_2O$.

Sulphate.—Dissolve 1 gm. in water, add concentrated hydrochloric acid, and boil until the solution is clear. Dilute and test with barium chloride solution. Where the amount is excessive it is desirable to filter off and weigh the precipitated barium sulphate. $BaSO_4 \times 1{\cdot}231 = ZnSO_4.7H_2O$; $BaSO_4 \times 0{\cdot}6916 = ZnSO_4$.

Zinc Peroxide, $ZnO_2 = 97{\cdot}4$. (ZnO, 83·56; Available Oxygen, 16·44.)—Insoluble in water, but soluble in dilute acids with evolution of oxygen (chlorine in the case of hydrochloric acid).

Determination of Zinc. — As given under Zinc Acetate. $ZnO \times 0{\cdot}8034 = Zn$.

Available Oxygen.—Dissolve 2 gm. of potassium iodide in 200 cc. of water, add 0·4 gm. of the sample of zinc peroxide and 25 cc. of dilute sulphuric acid. Allow to stand fifteen minutes and titrate the liberated iodine with $N/10$ sodium thiosulphate. 1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}0008$ gm. available oxygen or 0·004869 gm. ZnO_2.

Impurities.—As given under Zinc Acetate.

Arsenic.—As under Zinc Carbonate. Limit, 10 parts per million.

Other Metals.—As under Zinc Acetate, after solution in hydrochloric acid.

Zinc Phenolsulphonate (Zinc "sulpho-carbolate"), $Zn(C_6H_5OSO_3)_2.8H_2O = 555{\cdot}8$. ($Zn$, 11·76; $C_6H_5OSO_3$, 62·30; H_2O, 25·94.)—Solubility in water, 37; in alcohol, 60.

Determination of Zinc.—As under Zinc Acetate. $ZnO \times 0{\cdot}8034 = Zn$.

Phenol Sulphonate.—Dissolve 0·2 gm. in 50 cc. of water, and add 50 cc. of $N/10$ bromide-bromate mixture and 5 cc. of conc. hydrochloric acid. Shake during fifteen minutes, add 2 gm. of potassium iodide in 5 cc. of water, and titrate with $N/10$ thiosulphate. 1 cc. $N/10$ $Br \equiv 0{\cdot}006946$ gm. $Zn(C_6H_5OSO_3)_2.8H_2O$.

Impurities.—As under Zinc Acetate.

Zinc Phosphide, $Zn_3P_2 = 258{\cdot}19$. (Zn, 75·99; P, 24·01.)—Insoluble in water or alcohol; with dilute acids (except nitric) phosphine is evolved; nitric acid converts it into phosphate.

Determination of Zinc.—Dissolve 0·2 gm. in a little dilute hydrochloric acid and dilute to 50 cc. Add a solution of sodium carbonate solution drop by drop until the liquid remains slightly turbid after shaking; boil; add phenolphthalein, and continue the addition of the sodium carbonate solution until the liquid remains pink. Filter whilst hot and wash the precipitate thoroughly with hot water. Dry, ignite, and weigh as zinc oxide. $ZnO \times 0{\cdot}8034 = Zn$; $ZnO \times 1{\cdot}0577 = Zn_3P_2$.

Phosphorus.—Place 0·2 gm. in a conical flask, cover with a few cc. of water and add bromine water drop by drop with frequent shaking until a moderate excess of bromine is present. Add 5 cc. of dilute nitric acid, and boil until all the bromine has been evolved and no more residue is dissolved. Filter, add excess of molybdic acid solution to the filtrate and allow to stand for some hours on a warm plate. Filter, dissolve the precipitate in 3 per cent. ammonia, nearly neutralise with hydrochloric acid and precipitate the phosphate as under Sodium Phosphate. $Mg_2P_2O_7 \times 0{\cdot}2787 = P$.

Zinc Stearate.—Zinc stearate is a fine, white powder, insoluble in water, alcohol, or ether.

Determination of Zinc.—Boil 1 gm. with 50 cc. of *N*/10 sulphuric acid for ten minutes, cool, and titrate back with *N*/10 potassium hydroxide to methyl red. 1 cc. *N*/10 $H_2SO_4 \equiv 0{\cdot}004069$ gm. ZnO. The U.S.P. requires zinc stearate to contain not less than 13 per cent. or more than 15·5 per cent. of zinc oxide.

Impurities.—Zinc stearate almost invariably contains sulphate, which may be tested for by boiling with dilute hydrochloric acid, separating the liberated fatty acid and testing with barium chloride in the usual way. The melting-point of the liberated fatty acids should not be below 56° C. according to the U.S.P., but more usually it is found to be about 54° C.

Zinc Sulphate, $ZnSO_4.7H_2O=287{\cdot}5$. (Zn, 22·73; SO_4, 33·41; H_2O, 43·86.)—Solubility in water, 150; in glycerin, 35; insoluble in alcohol. Five molecules of water of crystallisation are lost at 50° C., the sixth at 100° C., and the seventh at 240° C.

Determination of Zinc.—As under Zinc Acetate or Zinc Phosphide. $ZnO \times 0{\cdot}8034 = Zn$; $ZnO \times 1{\cdot}984 = ZnSO_4$; $ZnO \times 3{\cdot}533 = ZnSO_4.7H_2O$.

Sulphate.—As under Sodium Sulphate. $BaSO_4 \times 0{\cdot}6902 = ZnSO_4$; $BaSO_4 \times 1{\cdot}2319 = ZnSO_4.7H_2O$.

Impurities.—As under Zinc Acetate.

Arsenic.—By the general method on 2 gm. Limit, 10 parts per million.

Other Metals.—As under Zinc Acetate.

Zinc Valerianate, $Zn(C_5H_9O_2)_2.2H_2O=303{\cdot}6$. (Zn, 21·53; $C_5H_9O_2$.66·60; H_2O, 11·87.)—Solubility in water, 1; in alcohol, 2; in ether, 0·2.

Determination.—The zinc may be determined as under Zinc Acetate. $ZnO \times 0{\cdot}8034 = Zn$; $ZnO \times 3{\cdot}731 = Zn(C_5H_9O_2)_2.2H_2O$.

Impurities.—As under Zinc Acetate.

Arsenic.—As under Zinc Benzoate. Limit, 10 parts per million.

Other Metals.—As under Zinc Acetate.

PART III

ORGANIC CHEMICALS.

Acetaldehyde, $CH_3.CHO$. M.W.=44·04.

Properties.—A colourless or slightly yellow, mobile liquid, with a characteristic odour, miscible in all proportions with water, alcohol, or ether. S.G., 0·789; B.Pt., 21° C. Residue on evaporation on the water bath not more than 0·02 per cent. Acidity not more than 0·5 per cent. (as acetic acid) when titrated with $N/10$ sodium hydroxide to phenolphthalein. 1 cc. $N/10$ $NaOH \equiv 0{\cdot}006$ gm. $CH_3.COOH$.

Determination.—Prepare a sodium sulphite solution by dissolving 12·6 gm. of anhydrous sodium sulphite in 400 cc. water, adding 100 cc. N sulphuric acid, diluting to 1000 cc. with 96 per cent. alcohol, and filtering after twenty-four hours. Weigh a few cc. of 96 per cent. alcohol in a weighing bottle, add 1 cc. of the aldehyde and repeat the weighing. Wash the solution into a 100 cc. flask, and make up to 100 cc. with alcohol. Pipette 10 cc. of this solution into a 100 cc. stoppered flask, mix with 50 cc. of the sulphite solution, and make up to 100 cc. with 50 per cent. alcohol. Carry out a blank experiment at the same time, omitting the aldehyde. After heating at 50° C. for at least four hours, withdraw 50 cc. from each flask and determine the sulphurous acid by means of $N/10$ iodine solution. The difference between the two titrations multiplied by two gives the volume of N iodine required by the original weight of aldehyde. 1 cc. N I $\equiv 0{\cdot}0220$ gm. $CH_3.CHO$.

Acetanilide (*Antifebrin*), $C_6H_5NH.COCH_3$. M.W.=135·1.

Properties.—Colourless, glistening crystalline plates. M.Pt., 113° to 113·5° C.; B.Pt., 263° C.

Ash, less than 0·1 per cent.

Solubility in water, 0·5; in boiling water, 5; in alcohol, 23; in ether, 2·8; in chloroform, 10.

Tests.—It should give a positive reaction with the isonitrile test, and the aqueous solution should give a white precipitate with bromine water. The cold aqueous solution should be neutral and not affected by ferric chloride solution, nor should it discharge the colour of potassium permanganate solution.[1]

Acetannin (*Tannigen*; Di-acetyl tannic acid), $C_{14}H_8O_9.(CO.CH_3)_2$. M.W.=406·1.

[1] For methods of determination see A. Seidell, *J. Amer. Chem. Soc.*, **29**, 1907, 1091 (Abs. *J. Soc. Chem. Ind.*, 1907, **26**, 989); J. L. Turner and Vanderkleed, *Amer. J. Pharm.*, 1907, **79**, 151 (Abs. *Y.B.P.*, 1907, 4); Reclaire, *Perf. & Ess. Oil. Rec.*, 1921, **12**, 280.

Properties.—Pale yellow, odourless, hygroscopic powder, almost insoluble in water; soluble in alcohol. It melts with decomposition at 187 to 190° C.

Tests.—Acetannin is decomposed by heating with alkali into tannate and acetate. It should be free from ash.

Acetic Acid, CH_3COOH. M.W.=60·06.

Properties.—Glacial acetic acid is a colourless, mobile liquid, with a pungent odour, miscible in all proportions with water, alcohol, ether, and chloroform. It is often frozen to a glassy mass in the colder weather. No weighable residue should be left on evaporation. B.Pt. 118° C.; S.G. 1·056.

Determination.—The strength of the acid may be best determined from its solidifying point, using the following table:—

Solidifying Point, ° C.	Acetic Acid.
16·70	100·0 per cent.
16·65	99·5 ,,
14·80	99·0 ,,
14·00	98·5 ,,
13·25	98·0 ,,
11·95	97·0 ,,

The B.P. requires not less than 98·9 per cent. acetic acid. In the case of the more dilute acids, the percentage of acetic acid may be determined by titrating with $N/2$ sodium hydroxide to phenolphthalein. 1 cc. $N/2$ $NaOH \equiv 0{\cdot}03003$ gm. CH_3COOH.

Common Impurities are chlorides, sulphates, nitrates, sulphites.

Permanganate Test.—2 cc. of 33 per cent. acid added to 3 drops of $N/10$ permanganate in 10 cc. of water should not decolorise the liquid in thirty seconds. On neutralising the acid with pure ammonia no tarry odour should be observed.

Formic Acid.—Add 1 gm. of sodium acetate to 10 cc. of a 10 per cent. solution, and heat with mercuric chloride solution for half an hour on the water bath; no precipitate should be obtained.

Arsenic.—By the general method, using 5 gm. Allowable limit, 2 parts per million.

Heavy Metals.—Neutralise 10 cc. of 33 per cent. acid with ammonia and add 2 drops of sodium sulphide solution; no darkening should be produced.

B.P. Strengths.—Acetic acid B.P. contains 33 per cent. acetic acid (S.G. 1·044), and acetic acid, diluted B.P., contains 5 per cent. acetic acid (S.G. 1·007).

Acetic Anhydride, $(CH_3CO)_2O$. M.W.=102·07.

Properties.—A colourless, mobile liquid, with a suffocating smell. B.Pt., 137° to 138° C.; S.G. 1·085. 10 gm. on evaporation should not leave any residue.

Determination.—(i) Run into a weighed stoppered bottle containing 10

to 20 cc. of water about 2 cc. of the anhydride, weigh and allow to stand several hours; dilute to about 200 cc. and titrate with *N* sodium hydroxide to phenolphthalein. This gives total acidity due to free acetic acid and acetic acid due to anhydride. (ii) Measure into a weighed stoppered vessel containing 10 to 20 cc. of recently distilled aniline about 2 cc. of the anhydride, mix, cool and weigh. Wash into 200 cc. of cold water and titrate as before. This gives the acidity due to free acetic acid together with half the acetic acid due to the anhydride. Subtract the second titration from the first and double the result, allowing for the different weights taken. 1 cc. *N* NaOH ≡ 0·05104 gm. $(CH_3CO)_2O$.[1]

Common Impurities are heavy metals, chlorides, sulphates, phosphorus compounds, and higher homologues. Phosphorus compounds may be tested for by boiling with dilute nitric acid (S.G. 1·05), and testing for phosphate with ammonium molybdate. Higher homologues are indicated by a foreign odour when a small quantity, dissolved in water, is nearly neutralised with sodium hydroxide.

Acetone, CH_3COCH_3. M.W.=58·06.

Properties.—A colourless, mobile, inflammable liquid with a characteristic odour. B.Pt. 56° C.; S.G. 0·798. Miscible in all proportions with ether, alcohol, and water. No residue should be left on evaporation of 20 cc.

Tests.—The B.P. requires that not less than 95 per cent. shall distil between 55° and 57° C., and that 10 cc. shall not require more than one drop of *N* NaOH to give a pink colour with phenolphthalein. 1 drop of *N*/10 permanganate should not be decolorised by 10 cc. in thirty minutes. It should yield a clear mixture with an equal volume of petroleum ether. 0·1 cc. of N/10 NaOH should produce a pink colour with phenolphthalein when added to 10 cc. diluted with water.

Determination.—Modified Messinger's Method.[2]—An amount of acetone in aqueous solution equivalent to 30 to 40 mg. is pipetted into 50 cc. of *N* sodium hydroxide contained in a glass bottle with a glass stopper. After standing for five minutes about 25 per cent. excess of *N*/10 iodine solution is run in from a burette with continual shaking, keeping the liquid in rapid rotation. The bottle is then stoppered, and the solution allowed to stand for at least ten minutes (twenty minutes in cold weather). 25 cc. of 2*N* sulphuric acid are then added, 0·3 to 0·4 cc. being added in excess of the amount necessary to neutralise the 50 cc. of sodium hydroxide solution. *N*/20 sodium thiosulphate is then added from a burette until the yellow colour just remains visible, the titration being completed to starch paste. 1 cc. *N*/10 iodine ≡ 0·9675 mg. acetone.

Acetyl Bromide, CH_3COBr. M.W.=122·9.

Properties.—A colourless, pungent, fuming liquid; sometimes slightly yellow. B.Pt. 81° C. S.G. 1·52 at 9·5° C.

Common Impurities are phosphorus and sulphate, tested for as under Acetyl Chloride.

Determination.—As under Acetyl Chloride. Percentage $CH_3COBr = 6{\cdot}825(a + b - 100) = x$. Percentage $HBr = a - 0{\cdot}6582x$. Percentage $CH_3COOH = b - 0{\cdot}4883x$.

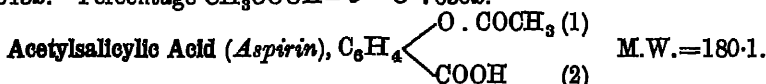
Acetyl Chloride, CH_3COCl. M.W.=78·48.

[1] Radcliffe and Medofski, *J. Soc. Chem. Ind.*, 1917, **36**, 628; see also Terlinck, *Ingenieur Chimiste*, 1925, **9**, 140 (Abs. *Chem. Abs.*, 1927, 1947).
[2] Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39.

Properties.—A colourless, pungent, fuming liquid; sometimes slightly yellow. B.Pt. 51° C.; S.G. 1·130 at 0° C., 1·105 at 20° C.

Common Impurities are phosphorus and sulphate. 1 to 2 cc. boiled with nitric acid (S.G. 1·19) should not give any reaction for phosphates with ammonium molybdate. A small quantity dissolved in water should give no precipitate with barium chloride.

Determination.—Weigh a stoppered flask containing 50 cc. of N NaOH, add about 2 cc. of the sample, cool and re-weigh. Titrate the excess of alkali against N H_2SO_4, using phenolphthalein (T_1). Dilute the neutralised liquid with water to 500 cc. and titrate 50 cc. of this against $N/10$ $AgNO_3$ (T_2). Calculate the latter titration to percentage of HCl, $=a$, and the difference between the two titrations (*i.e.* T_1 and T_2) to percentage of CH_3COOH, $=b$. Then percentage $CH_3COCl=4{\cdot}357\ (a+b-100)=x$. Percentage HCl$=a-0{\cdot}4645x$. Percentage $CH_3COOH=b-0{\cdot}7650x$.


Acetylsalicylic Acid (*Aspirin*), $C_6H_4\langle^{O\,.\,COCH_3\ (1)}_{COOH\ \ (2)}$ M.W.=180·1.

Properties.—A white, crystalline powder with a slight acid taste. M.Pt. 135° to 137° C. (the B.P. gives 133° to 135° C.). The melting-point should be determined by heating the bath to about 125° C., then placing the tube in position and continuing as usual. Prolonged heating hydrolyses the acid and lowers the M.Pt. Ash not more than 0·1 per cent. Solubility in cold water, 0·3 (decomposed by hot water); in alcohol, 24. Soluble in ether.

Determination.—1·5 gm. is boiled with 50 cc. of $N/2$ NaOH for ten minutes and titrated back with $N/2$ hydrochloric acid to phenolphthalein. 1 cc. $N/2$ NaOH $\equiv$ 0·04505 gm. $C_6H_4O\,.\,COCH_3\,.\,COOH$. Free salicylic acid may be detected by dissolving 0·2 gm. in 5 cc. of alcohol, diluting to 50 cc. with water and adding 1 cc. of iron-alum solution—no violet coloration should appear. This test is extremely delicate and its importance may be exaggerated; moreover, it may easily be rendered useless by the addition of small amounts of citrates, etc., to the acetylsalicylic acid.[1]

Aconitine, $C_{34}H_{47}NO_{11}$. M.W.=645·4.

Properties.—An alkaloid obtained from aconite root. Colourless, transparent crystals. Aconitine, when heated rapidly, melts at 197° to 198° C.; but if slowly heated, melting may take place anywhere between 182° and 200° C. Solubility in benzene, 17·85 at 25° C.; in ether, 2·27 at 25° C.; in absolute alcohol, 2·7 at 22° C.; in water, 0·031 at 25° C.; in petroleum ether, 0·028 at 25° C. Soluble in chloroform; very slightly soluble in carbon disulphide.

Tests.—Aconitine gives the usual alkaloid reactions; there are no satisfactory specific colour tests. It gives rise to a tingling and numbing sensation when placed on the tongue in extremely high dilution, the effect being sensible in 1 in 100,000 solution of the pure alkaloid. (This test should be performed with great care.) Aconitine forms a series of crystalline salts, but is almost invariably used as the free alkaloid. It readily undergoes hydrolysis with acids or alkalis. An aqueous solution of about 1 in 500 strength, slightly acidified with acetic acid, gives a crystalline precipitate with a few drops of $N/10$ potassium permanganate solution. The crystals are seen to be of characteristic form when examined under the microscope.

[1] For the further examination, see A. J. Jones, *C. & D.*, 1919, **91**, 402; A. Nutter Smith, *Y.B.P.*, 1920, 421; *Analyst*, 1920, **45**, 412.

Acriflavine (Flavine; Trypaflavine), $(C_6H_3NH_2)_2.CH.N.(CH_3Cl).HCl$. M.W.=296·0. Acriflavine is 3 : 6-diamino-10-methyl-acridinium chloride. It occurs as a brownish-red crystalline powder, soluble in water and alcohol. The solubility in water varies in commercial samples. The alcoholic solution is yellow, with a green fluorescence. When the aqueous solution is treated with sodium hydroxide solution an orange precipitate is thrown down which almost entirely dissolves on heating. The ash should be negligible.

Adrenaline (Adrenine; Epinephrine; *l*-Methylaminoethanol-catechol, $C_6H_3(OH)_2CHOH.CH_2NH.CH_3$. M.W.=183·1.

Properties.—Adrenaline is an active principle obtained from the suprarenal gland. It has also been produced synthetically. It occurs as a white or buff-coloured powder. It is usually sold as a dilute solution of the hydrochloride. Adrenaline, though stable in the form of powder, is very easily decomposed in solution, and is particularly sensitive to alkalis. The synthetic compound is slightly soluble in water and easily dissolves in dilute acids. It melts with decomposition at 211° to 212° C.

Tests.—A small quantity of the solution when mixed with excess of sodium hydroxide solution gradually develops a characteristic unpleasant odour, this test being a very sensitive one. On adding ferric chloride solution to a solution of the base, an emerald green colour is produced, which is changed to purple by carefully adding a dilute sodium hydroxide solution.

Aloin.—A yellow, acicular crystalline substance extracted from aloes; odourless; solubility in water, 0·83; in alcohol, 5·55; almost insoluble in ether. Aloin is rapidly decomposed in alkaline solution and dissolves in dilute ammonia, giving a red solution with a green fluorescence. It should contain not more than 1·5 per cent. of matter insoluble in water. The ash should not be more than 0·5 per cent.

Insoluble Matter.—1 gm. dissolved in 150 cc. of water by shaking during two hours, filtered on a tared filter, and washed with 25 cc. of water should not leave more than 1·5 per cent. of insoluble matter (U.S.P.).

Amidopyrin (*Pyramidon*; Dimethylaminophenazone), $C_{13}H_{17}N_3O$. M.W. =231·2.—Small, colourless crystals. M.Pt. 108° C. Solubility in water, 9. Soluble in alcohol and ether.

Determination.—Amidopyrin may be determined in the same way as phenazone, by Lemaire's picric acid method. Dissolve 0·231 gm. of the sample in 10 cc. of water and add 40 cc. of $N/20$ picric acid solution (11·45 gm. per litre). After shaking for some minutes, filter the mixture and titrate the excess of picric acid in 25 cc. of the filtrate with $N/10$ caustic potash to methyl red. If n cc. of $N/10$ KOH are used, the percentage of amidopyrin is 20 $(10-n)$.

Tests.—Ferric chloride added to the solution produces a colour which is blue by reflected light and violet by transmitted light. Silver nitrate solution gives at first a bluish colour, which darkens, with separation of silver. Amidopyrin may be distinguished from phenazone by the fact that phenazone when treated with potassium nitrite and sulphuric acid gives a green to greenish-blue colour, whereas the amidopyrin gives a bluish-violet colour.

Aminoacetic Acid (Glycine; Glycocoll), $NH_2.CH_2.COOH$. M.W.= 75·05.—A white, crystalline powder with a sweetish taste. M.Pt. 240° C.; S.G. 1·16. Solubility in water, 23; in alcohol, 0·2.

Common Impurities are mineral residue, chloride, sulphate, ammonia.

Determination.—Dissolve about 0·3 gm. in water, add 10 cc. of neutral formaldehyde solution and 100 cc. of neutral alcohol, and titrate the acidity with $N/10$ NaOH to phenolphthalein. 1 cc. $N/10$ NaOH ≡ 0·007505 gm. $NH_2.CH_2COOH$.

Amyl Acetate, $C_7H_{14}O_2$. M.W.=130·1.—Amyl acetate is a colourless liquid with a fruity odour. It consists of a mixture of esters, but chiefly *iso*amyl acetate. S.G. about 0·878; boiling range, 135° to 145° C. Pure *iso*amyl acetate has S.G. 0·885 and boils at 148° C.

Determination.—The following are determined:

Free Acid.—Titrate 5 gm. dissolved in neutral alcohol with $N/10$ sodium hydroxide to phenolphthalein. 1 cc. $N/10$ NaOH ≡ 0 006006 gm. CH_3COOH.

Amyl Acetate.—Saponify 1 gm. with 25 cc. of $N/2$ alcoholic potassium hydroxide. 1 cc. $N/2$ KOH ≡ 0·06508 gm. $C_7H_{14}O_2$.

Amyl Alcohol.—Shake 20 cc. in a graduated cylinder with a mixture of 10 cc. of glacial acetic acid and 10 cc. of water. If any contraction occurs it is due to amyl alcohol, which is soluble in 50 per cent. acetic acid.

Amyl Alcohol (*Iso*amyl Alcohol; *Iso*butyl Carbinol), $(CH_3)_2CH.CH_2.CH_2OH$. M.W.=88·12.—This is a clear, colourless liquid, having a characteristic odour, consisting chiefly of inactive *iso*amyl alcohol. S.G. 0·814; B.Pt. 131° C. Solubility in water, 2·3; miscible in all proportions with alcohol and ether. Commercially pure amyl alcohol (B.Pt. 128° to 132° C.) consists of a mixture of varying proportions of *iso*butyl carbinol with active amyl alcohol. 10 cc. should leave no residue on evaporation.

Common Impurities.—When shaken with an equal volume of conc. sulphuric acid it should show only a slight darkening. The substance should be completely soluble in an equal volume of hydrochloric acid and should show no oily globules when 2 cc. are treated by the Gerber test, as for fat in milk. When dilute (about 1 per cent.) sulphuric acid which has been shaken with 25 to 50 cc. of the alcohol is distilled with excess of sodium hydroxide into standard acid, little ammonia, if any, should be indicated.

Amyl Nitrite, $(CH_3)_2CH.CH_2.CH_2.NO_2$. M.W.=117·1.—A clear, yellow, fragrant liquid. B.Pt. 96° C. The B.P. requires that 90 per cent. should distil below 100° C. This is not easily attainable and 80 per cent. is a better limit. S.G. 0·870 to 0·880 (B.P.). Insoluble in water, but miscible with alcohol and ether in all proportions.

Determination.—Dilute 5 gm. to 100 cc. with 90 per cent. alcohol and determine as under Spiritus Aetheris Nitrosi (p. 277). 1 cc. NO at N.T.P. ≡ 0·005242 gm. $C_5H_{11}NO_2$. The B.P. requires not less than 82·8 per cent., the U.S.P. 80 per cent. Amyl nitrite should not become turbid on cooling to 0° C., showing the absence of water.

Amylocaine Hydrochloride (*Stovaine*; Benzoyl-dimethylamino-methyl methylethyl-carbinol hydrochloride), $(CH_3)_2N.CH_2.C(CH_3)(C_2H_5).O.CO.C_6H_5.HCl$. M.W.=271·7.—A white, crystalline powder or white scales. Solubility in water, 7. Soluble in alcohol. M.Pt. 175° C.

Aniline, $C_6H_5.NH_2$. M.W.=93·1.—A colourless, oily liquid, with characteristic odour. It slowly turns brown on exposure to air. M.Pt. 6° C.; B.Pt. 184° C.; S.G. 1·0267. Solubility in water, 3·1. Aniline dissolves water to the extent of 4·5 parts in 100 parts of aniline.

Determination.—This is carried out by Sanderson and Jones[1] by a determination of the freezing-point. They state that pure aniline has a freezing-point of 6° C., and that the presence of any ordinary impurities will lower this figure.

Tests.—Mix 10 cc. of the oil with 50 cc. of water and 40 cc. of hydrochloric acid. A perfectly clear solution, without odour, should be obtained.

Apomorphine Hydrochloride, $(C_{17}H_{17}O_2N.HCl)_2H_2O$. M.W.=625·2.—Contains apomorphine, 85·7 per cent.; water, 2·9 per cent. Forms small white or greyish shining prisms. Solubility in water, 1·7. The solution when freshly made should not have an emerald-green colour. A 1 in 500 solution gives a deep red-brown precipitate with gold chloride solution which, on examination under the microscope, is found to consist of small, fine, needle-shaped crystals. One drop of aqueous ammonia added to 5 cc. of apomorphine solution produces a green colour, and when further shaken with chloroform a violet lower layer is given. This test may be used for detecting apomorphine in morphine.

β-Chloro-morphide.—This occasional impurity may be detected by the following test: Dissolve 0·1 gm. of apomorphine in 10 cc. of water and add 5 cc. of saturated sodium bicarbonate solution. Extract with 20 cc. of ether, separate, and shake the ethereal solution three times with 20 cc. of water. Evaporate the ethereal solution to dryness and treat the residue with 5 cc. of nitric acid containing 0·5 per cent. of silver nitrate. After standing ten minutes, heat for an hour on the water bath, keeping up the volume by adding water. No appreciable precipitate of silver chloride should be formed.

Arsenobenzene (*Salvarsan; Kharsivan;* Arsphenamine (U.S.P.); 3:3′—Diamino-4:4′—dihydroxy-arsenobenzene hydrochloride). $HCl.NH_2(OH).C_6H_3.As : As.C_6H_3(OH)NH_2.HCl$. M.W.=475·1.—A yellow, crystalline, hygroscopic powder, very unstable in air, containing 31·55 per cent. of arsenic. Solubility in water, 20; in alcohol, 8.

Determination.—

Arsenic.[2]—Dissolve 0·5 gm. in 10 cc. of water, add 5 cc. of nitric acid, heat, and add ammonium persulphate in lumps until the solution is colourless and clear. If the decomposition is troublesome add a few cc. of water and several gm. of persulphate all at once and boil. Make up to 100 cc., add 5 cc. of saturated sodium ammonium hydrogen phosphate solution, and then magnesia mixture in excess (about 40 cc.). If a precipitate forms, dissolve in dilute nitric acid, maintain at the boiling-point, then add a decided excess of ammonia in the usual manner, cool, allow to stand about two hours, filter and wash with dilute ammonia. The precipitate may be weighed as magnesium pyro-arsenate, or dissolved in 70 cc. of dilute hydrochloric acid (3 vols. acid to 2 vols. water) and shaken until the precipitate is dissolved. Cool, add 3 gm. of potassium iodide in 6 cc. of water, rotating for one minute; then add 70 cc. of water and titrate at once with *N*/10 thiosulphate. Not less than 30 per cent. and not more than 34 per cent. of arsenic should be found. 1 cc. *N*/10 $Na_2S_2O_3 \equiv 0{\cdot}003748$ gm. As. The U.S.P. method is as follows: Place about 0·2 gm. of arsphenamine, accurately weighed, in a glass-stoppered 200 to 300 cc. flask. Add 1 gm.

[1] *J. Soc. Chem. Ind.*, 1920, **39**, 87.
[2] Rogers, *Can. Chem. J.*, 1919, **3**, 298; see also Contardi and Cazzani, *Boll. Chim. Farm.*, 1926, **65**, 513; Sensi, *Ann. Chim. Appl.*, 1926, **16**, 491.

of finely powdered potassium permanganate and 5 cc. of diluted sulphuric acid, and allow to stand for ten minutes, rotating the contents of the flask during this time to ensure thorough mixing. Add 10 cc. of conc. sulphuric acid in portions of about 2 cc., rotating the flask after each addition. When the reaction has ceased, add sufficient hydrogen peroxide (10 vols.) to dissolve the brown precipitate completely (about 5 to 7 cc.). Towards the end of the reaction the hydrogen peroxide is to be added drop by drop to avoid any great excess. Dilute with 25 cc. of distilled water and boil gently over an asbestos wire gauze for from fifteen to twenty minutes, or until the excess of hydrogen peroxide is expelled. Dilute with 50 cc. of distilled water, and add *N*/10 potassium permanganate until the liquid is faintly pink, then discharge the pink colour by the addition of a drop of *N*/10 oxalic acid. Cool the solution, add 2·5 gm. of potassium iodide, stopper the flask tightly, and allow it to stand in a cool, dark place for one hour. Then titrate the liberated iodine with *N*/10 sodium thiosulphate without the use of starch indicator. Make a blank test with the same quantities of the reagents, and correct the assay for the volume of *N*/10 sodium thiosulphate used in the blank. Each cc. of *N*/10 sodium thiosulphate corresponds to 0·003748 gm. of As.

Tests.—The ash should not be more than 0·5 per cent. If 0·5 gm. of the powder is added to 35 cc. water, the powder should rapidly dissolve. This solution should be neutral to bromophenol blue and should be free from suspended particles. The addition of 1 cc. of 15 per cent. sodium hydroxide solution should cause a preliminary separation of solid arseno base, which, on shaking, should completely dissolve, forming a bright yellow solution. This, on dilution to 250 cc. with 0·5 per cent. saline solution, should give a perfectly bright, light-yellow liquid. An aqueous solution (1 in 100) is precipitated by mercuric potassium iodide solution. Novarsenobenzene is not precipitated by this reagent.

Atropine (*dl*-Hyoscyamine), $C_{17}H_{23}NO_3$. M.W.=289·2.—Colourless crystals or a white, crystalline powder. A solution of atropine in alcohol is optically inactive. M.Pt. 114·5° to 115·5° C. (B.P.); when pure it melts at a slightly higher temperature, but the presence of hyoscyamine lowers this figure. Solubility in water, 0·22 at 25° C.; in alcohol, 68·4 at 25° C.; in chloroform, 64·1 at 25° C.; in ether, 6·0 at 25° C.

Determination.—Dissolve 0·6 gm. in 25 cc. of *N*/10 hydrochloric acid, and titrate back with *N*/10 alkali to bromophenol blue until a distinct blue colour is formed. 1 cc. *N*/10 HCl ≡ 0·02892 gm. atropine.

Tests.—

Aurichloride.—Dissolve 0·05 gm. in 5 cc. of water, make acid with hydrochloric acid, and add a little auric chloride solution. A yellow precipitate separates as oily drops, and subsequently crystallises. After recrystallising from boiling water acidified with hydrochloric acid, the M.Pt. is 137° to 139° C.

Picrate.—Add a few cc. of saturated picric acid solution to a solution of atropine in dilute hydrochloric acid. The crystals may be recrystallised from acetone, and melt at 175° to 176° C.

Wagner's Reagent.—Atropine and its salts form a precipitate in very dilute solutions with Wagner's reagent (see Appendix), which when examined microscopically is found to consist of small rods or triangular plates of characteristic form.

Vitali's Test.—Evaporate 0·01 gm. to dryness on a water bath with 5 drops of nitric acid and moisten the residue after cooling with freshly prepared alcoholic potassium hydroxide solution. A violet colour is produced. This colour is also formed by hyoscyamine and by hyoscine, while veratrine, strychnine, and *pseudo*-aconitine give similar colours. Homatropine does not answer to this test.

Atropine Sulphate, $(C_{17}H_{23}O_3N)_2.H_2SO_4.H_2O$. M.W.=694·5.—Contains atropine, 83·3 per cent.; water, 2·6 per cent. A white, crystalline powder. M.Pt. 194° C. Solubility in water, 263 at 25° C.; in alcohol, 27 at 25° C.

Tests.—Atropine sulphate responds to the tests given under atropine (*q.v.*).

Barbitone (*Veronal*; Malourea; Diethylbarbituric Acid), $C_8H_{12}N_2O_3$. M.W.=184·1.—A white, crystalline powder. M.Pt.[1] 191° C. when dry (B.P.); 187° to 190° C. (U.S.P.). Solubility in water, 0·62; in 90 per cent. alcohol, 11·7; in ether, 8·7.

Tests.—Millon's reagent (see Appendix), with a saturated aqueous solution acidified with dilute nitric acid, produces a white precipitate soluble in excess of the reagent. The ash should be inappreciable.

Determination.[2]—Dissolve 0·3 gm. in 10 cc. of 2 per cent. sodium hydroxide solution saturated with salt. Add 2 cc. of conc. hydrochloric acid and 5 cc. of water. Extract five times with 30, 20, 20, 10 and 10 cc. of a solvent composed of 20 cc. of alcohol, 10 cc. of ether, and 70 cc. of chloroform. Wash the combined extracts with 2 cc. of water acidified with a drop of hydrochloric acid. Filter through a pledget of cotton into a small weighed beaker. Evaporate off the solvent, dry for ten minutes in a steam oven, and weigh.

Beberine Sulphate.—Beberine is an alkaloid obtained from *Nectandra Bebeeru*, or Greenheart bark. It occurs as brown, translucent scales, very soluble in water, and having a very bitter taste. There are no distinctive tests for this alkaloid. It must be distinguished from berberine sulphate. The B.P. gives 189° to 190° C. as the M.Pt., but this is lower than that given by the pure, dry salt.[3]

Benzaldehyde, $C_6H_5.CHO$. M.W.=106·1.—Colourless, or slightly yellow, highly refractive liquid, miscible with alcohol or ether. S.G. 1·050 to 1·052. Refractive Index (20° C.), 1·545. B.Pt. 179° to 180° C.

Determination of Hydrocyanic Acid.—Shake 0·5 cc. of benzaldehyde with 5 cc. of water, 0·5 cc. of sodium hydroxide solution, and 0·1 cc. of ferrous sulphate solution. Warm gently. Add a slight excess of hydrochloric acid—no blue colour should be formed.

Chlorine Compounds.—The U.S.P. test is as follows: Wind the end of a copper wire into a spiral about 6 mm. in diameter and 6 mm. long, and hold it in a non-luminous flame until it glows without colouring the flame green. Cool the wire, dip the spiral in the benzaldehyde, ignite, allow it to burn outside of the flame, and then bring the spiral into contact with the lower, outer edge of the non-luminous flame; not even a transient green colour is imparted to the flame in the absence of halogen compounds.

[1] Ferrey, *Pharm. J.*, 1927, **119**, 31.
[2] Glycart, *J. Ass. Off. Agr. Chem.*, 1924, **8**, 48.
[3] See Richmond, *Analyst*, 1918, **43**, 168.

Determination.—The U.S.P. requires not less than 85 per cent. of benzaldehyde. Dissolve about 3 cc. of freshly distilled phenylhydrazine in 60 cc. of alcohol, and titrate 25 cc. of the freshly prepared solution with $N/2$ hydrochloric acid to bromophenol blue. Add 25 cc. of the same solution to 1 gm. of benzaldehyde, and allow to stand for thirty minutes. Add bromophenol blue, acidify with a measured excess of $N/2$ acid, and add 20 cc. of water. Filter, and wash the precipitate with distilled water until the washings are neutral. Titrate the excess of hydrochloric acid with $N/2$ NaOH. 1 cc. $N/2$ HCl ≡ 0·053 gm. benzaldehyde.

Benzamine Hydrochloride (β-Eucaine Hydrochloride, Benzoyl-vinyl-diacetonalkamine Hydrochloride), $C_{15}H_{21}NO_2.HCl$. M.W.=283·6.—A white, crystalline powder. M.Pt. 268° C. with decomposition. Solubility in water, 2·5.

Tests.—A solution should give no precipitate with potassium iodide, showing the absence of α-eucaine. 0·1 gm. in 20 cc. of water yields with 4 drops of ammonia solution a precipitate which is redissolved on adding an equal volume of distilled water. The further addition of ammonia produces a precipitate again, which is dissolved on adding 10 cc. of distilled water. The precipitate given by α-eucaine is not redissolved.

Benzamine Lactate (β-Eucaine Lactate), $C_{15}H_{21}NO_2.C_3H_6O_3$. M.W.= 337·3.—A white, crystalline powder. Solubility in water, 25; in alcohol, 12.

Tests.—For tests, see Benzamine Hydrochloride, *supra*; see also Cocaine (p. 140).

Benzene, C_6H_6. M.W.=78·08.—A colourless, mobile, inflammable liquid. S.G. 0·883; B.Pt. 80·5° C. When cooled to 0° C. it solidifies, and does not melt under 4° C. This shows freedom from other hydrocarbons; the pure product melts at 5·4° C. The B.P. is satisfied with a product having S.G. 0·880 to 0·887, and of which 95 per cent. boils between 79° and 82° C. It should be free from fixed residue. Practically insoluble in water; miscible in all proportions with alcohol and ether.

Test for Carbon Disulphide.—Add 2 drops of phenyl hydrazine to 10 cc. of benzene, thoroughly shake during 1 to 1½ hours and allow to stand; a precipitate indicates the presence of carbon disulphide.

Thiophene.—Shake 20 cc. with 5 cc. of conc. sulphuric acid; no coloration should develop, and on further adding a crystal of isatin and continuing the shaking, no blue or green colour should be produced.

Benzoic Acid, C_6H_5COOH. M.W.=122·1.—A light, crystalline powder. Two varieties are known, the one obtained by sublimation from benzoin, the other synthetically prepared. The former has an aromatic odour, and is usually slightly yellow in colour, and the M.Pt. and B.Pt are lower than the synthetic product. M.Pt. 121·5° C. (from benzoin at 120° C.); B.Pt. 249° C. Solubility in water, 0·25; in alcohol, 46·7; in ether, 31·4.

Determination.—Titrate 0·3 gm. with $N/10$ sodium hydroxide to phenolphthalein. 1 cc. $N/10$ NaOH ≡ 0·012208 gm. C_6H_5COOH.

Tests.—It should not char on heating, and should sublime without residue.

Test for Chloride.—Heat the acid with twice its weight of calcium carbonate (free from chloride) in a crucible; no chloride should be found in the residue from the "natural" compound, and not more than traces from the synthetic compound.

Test for Cinnamic Acid.—Heat 1 gm. with 1 gm. of potassium perman-

ganate and 10 cc. of sulphuric acid (S.G. 1·07); a smell of benzaldehyde should not be evolved.

Test for Salicylic Acid.—Add ferric chloride solution to the aqueous solution and filter; no violet colour should be seen in the filtrate.

Benzyl Benzoate, $C_6H_5CO.OC_7H_7$. M.W.=212·1.—A pleasant smelling, crystalline mass, melting at 20° to 21° C. It is easily supercooled, and may be liquid at ordinary temperatures. B.Pt. 323° C.; S.G. at M.Pt. 1·122. Refractive Index (20° C.), 1·569 to 1·570. Saponification Value, 264.

Benzyl Succinate, $C_2H_4(CO.OCH_2C_6H_5)_2$. M.W.=298·2.—White, odourless crystals, soluble in alcohol, ether, or chloroform. M.Pt. 45° C. On saponification with alcoholic potassium hydroxide, benzyl alcohol and potassium succinate are formed.

Berberine, $C_{20}H_{17}NO_4$. M.W.=335·1.—A yellow, crystalline powder containing varying amounts of water of crystallisation, which cause the M.Pt. to be indefinite. Slightly soluble in water, alcohol, chloroform, and benzene; insoluble in ether and petroleum ether.

Tests.—Berberine forms characteristic crystals when treated in dilute solution with a solution of chromic acid or dilute hydrochloric acid, but the greater part of the precipitate is amorphous.

Berberine Sulphate, $C_{20}H_{17}NO_4.H_2SO_4$. M.W.=433·2.—Forms yellow crystals, slightly soluble in water, 0·6. Berberine Sulphate and Hydrochloride (solubility 0·2) are less soluble in water than the alkaloid itself.

Beta-Naphthol, $C_{10}H_7OH$. M.W.=144·1.—White, lustrous, crystalline plates, having a faint phenolic odour. M.Pt. 122° C.; B.Pt. 286° C. Solubility in cold water, 0·1; much more soluble in hot water; readily soluble in alcohol and ether, soluble in chloroform and fixed oils.

Determination.—Methods of determination have been suggested by Kuster,[1] Messinger and Vostmann,[2] and by Wilkie.[3]

Tests.—A cold, saturated aqueous solution should give no violet coloration with a solution of calcium hypochlorite (absence of α-naphthol). 1 gm. should dissolve without residue in 50 cc. of 10 per cent. ammonia solution, and the resulting solution should not have more than a pale yellow colour. The aqueous solution should be neutral. No residue should be obtained on ignition.

Beta-Naphthol Benzoate (Benzonaphthol), $C_{10}H_7C_7H_5O_2$. M.W.=248·1. —White, crystalline, odourless powder. M.Pt. 110° C. Almost insoluble in water or ether; soluble in alcohol or chloroform.

Tests.—0·2 gm. dissolves in 2 cc. of conc. sulphuric acid giving a pale yellow colour, and on diluting with 20 cc. of water and making alkaline with ammonia a strong greenish fluorescence appears.

Beta-Naphthol Salicylate (*Betol*), $C_6H_4OH.COOC_{10}H_7$. M.W.=264·1.—Odourless, white, shining crystals. M.Pt. 95° C. Insoluble in water, soluble in boiling alcohol or in ether.

Tests.—On shaking 0·1 gm. with alcohol and adding a drop of ferric chloride solution no purple colour should be formed, showing the absence of free salicylic acid. On adding 0·1 gm. to 3 cc. of sulphuric acid a lemon-yellow solution results which changes to olive green on adding a trace of nitric acid.

[1] *Ber.*, 1890, **23**, 2754. [2] *Ibid.*, 1890, **23**, 2754.
[3] *J. Soc. Chem. Ind.*, 1911, **30**, 398.

Brilliant Green (Tetraethyl-diamido-triphenyl carbinol sulphate).—Readily dissolves in water to a deep green solution. On reducing with zinc dust and dilute hydrochloric acid until colourless, and filtering a few drops on to a filter paper, the colour should not return immediately on exposure to the air, but should be restored by spotting with 1 per cent. chromic acid solution. Zinc should be absent.

Bromoform, $CHBr_3$. M.W.=252·8.—A heavy, mobile, colourless liquid. S.G. 2·83; B.Pt. 148° to 150° C. The U.S.P. IX allows the addition of 4 per cent. of absolute alcohol, which alters the S.G. to 2·59 to 2·62 at 25° C.

Brucine, $C_{23}H_{26}O_4N_2$. M.W.=394·2.—A white, crystalline powder, or colourless crystals. It contains four molecules of water of crystallisation. When anhydrous it melts at 178° C. Solubility in water, 0·1; in alcohol, 45 at 25° C.; in chloroform, 11·6 at 25° C.; in ether, 0·75.

Tests.—No immediate precipitate is formed by potassium ferrocyanide with an acid solution of brucine (distinction from strychnine). With a drop of nitric acid, a trace of the alkaloid produces a blood-red colour which on heating changes to yellow; if, after cooling, the mixture is treated carefully with stannous chloride solution a purple coloration is produced. A 1 in 1000 or even a 1 in 20,000 solution of brucine forms a crystalline precipitate with platinum chloride, which on microscopic examination is found to consist of a dense mass of rods.

Butyl-Chloral Hydrate (Trichlorbutylidene glycol), $CH_3.CHCl.CCl_2.CH(OH)_2$. M.W.=193·5.—Forms pearly white laminæ having a pungent odour. M.Pt. about 78° C. Solidifying point about 71° C. Solubility in water, 2·5; in alcohol, 160; in glycerin, 100; soluble in ether, chloroform, or fixed oils.

Tests.—No precipitate is given by a solution of the substance on adding a solution of silver nitrate.

Test for Chloral Hydrate.—Heat with a few drops of aniline and a little sodium hydroxide solution, when no odour of phenyl *iso*cyanide should be observed.

Caffeine, $C_8H_{10}N_4O_2.H_2O$. M.W.=212·1.—Contains 91·5 per cent. anhydrous caffeine. Forms colourless, silky, odourless needles. M.Pt. 235° C. (after drying). Caffeine loses not more than 8·5 per cent. of its weight when dried at 100° C. Solubility in water, 1·0; in alcohol, 1·5 at 25° C.; in chloroform, 12·9; in ether, 0·12.

Tests.—A saturated solution is not precipitated by *N*/10 iodine solution nor by Mayer's reagent, but gives a white precipitate with tannic acid, soluble in excess. On moistening a small crystal together with a crystal of potassium chlorate with hydrochloric acid and evaporating to dryness, a reddish residue remains which becomes purple when exposed to ammonia vapour. The ash should be inappreciable.

Caffeine Citrate, $C_8H_{10}N_4O_2.C_6H_8O_7$. M.W.=386·2. (Anhydrous caffeine content=50·3 per cent.).—A white, odourless powder; solubility in hot water, 25, but is dissociated on the further addition of water, with separation of caffeine.

Determination.—Dissolve 1·5 gm. in 100 cc. of water, and titrate with *N*/2 KOH to phenolphthalein. 1 cc. *N*/2 KOH ≡ 0·06437 gm. caffeine citrate. It may also be determined by dissolving 1 gm. in hot water, making alkaline with sodium hydroxide, extracting with chloroform, and

drying the residue at 100° C. Not less than 0·45 gm. should be obtained (B.P.). Caffeine citrate gives the reactions mentioned under caffeine.

Caffeine Hydrobromide, $C_8H_{10}N_4O_2.HBr.2H_2O$. M.W.=311·1 (Anhydrous caffeine content=62·4; water=11·6).—Large, transparent, colourless crystals; solubility in water, 2, with decomposition.

Determination.—Dissolve 0·5 gm. in 50 cc. of water, acidify with 5 cc. of dilute nitric acid, and add 20 cc. of *N*/10 silver nitrate. Titrate the excess of silver nitrate with *N*/10 thiocyanate. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·0311 gm. caffeine hydrobromide.

Caffeine.—Dissolve 1 gm. in 100 cc. of water, make alkaline with ammonia, and extract with six quantities each of 20 cc. of chloroform; evaporate the solvent, and dry the residue at 100° C. This residue should give the reactions of caffeine (*vide supra*).

Caffeine Salicylate, $C_8H_{10}N_4O_2.HC_7H_5O_3$. M.W.=332·3 (Anhydrous caffeine=58·4).—A white, crystalline powder, soluble in water or alcohol. It may be titrated, or the caffeine may be determined as under Caffeine Citrate. 1 cc. *N*/10 KOH ≡ 0·03323 gm. caffeine salicylate.

Caffeine Sodium Benzoate.—A white, amorphous powder, containing about 45 per cent. of caffeine. Solubility in water, about 50.

Determination: Caffeine.—Dissolve 1 gm. in 50 cc. of water, make alkaline with 25 cc. of *N*/2 sodium hydroxide, and extract with six quantities of 20 cc. of chloroform. Evaporate the chloroform, and dry the residue at 100° C. (see Caffeine Citrate).

Sodium Benzoate.—Add an excess of *N*/2 hydrochloric acid to the aqueous solution obtained as above, extract the benzoic acid with ether, and titrate the excess of acid with *N*/2 sodium hydroxide to bromophenol blue or methyl orange (*cf.* Sodium Benzoate, p. 102). 1 cc. *N*/2 HCl ≡ 0·07204 gm. sodium benzoate.

Caffeine Sodium Salicylate.—This is a similar product to caffeine sodium benzoate, and contains about 50 per cent. of caffeine. It may be tested in a similar way. 1 cc. *N*/2 HCl ≡ 0·08004 gm. sodium salicylate.

Caffeine Valerianate or **Valerate,** $C_8H_{10}N_4O_2.C_5H_{10}O_2$. M.W.=296·2 (Anhydrous caffeine content=65·5).—This salt occurs as a white powder, with an odour of valeric acid. It is easily decomposed by water or by heating. Caffeine may be determined as under Caffeine Citrate. The theoretical percentage of anhydrous caffeine is 65·5, but usually about 80 per cent. of caffeine is present.

Camphor, $C_{10}H_{16}O$. M.W.=152·2.—Occurs as colourless crystals, in pulverulent masses ("flowers" of camphor) or compressed in blocks. Camphor has a characteristic odour, and should be free from any safrol or terpene odour. M.Pt. about 175° C.; B.Pt. 204° C.; S.G. 0·990 to 0·995. A solution of 5 gm. in sufficient 90 per cent. alcohol to produce 20 cc. has an optical rotation of about +10°.[1] Schoorl[2] shows that the following formulæ apply between concentrations (C) of 5 and 25 per cent., and temperatures (t) between 10° C. and 30° C. In 70 per cent. alcohol, $[\alpha]_D$=33·8+0·2 C+0·09 t; in 90 per cent. alcohol, $[\alpha]_D$=37·05+0·145 C+0·09 t. Solubility in water, 1·4; in alcohol (96 per cent.), 156; in ether, 171; in olive oil, 25; in chloroform, 0·25. Synthetic camphor resembles

[1] For a full account of the rotation of camphor, see Portheil and van Noonen, *J. Soc. Chem. Ind.*, 1900, 684.

[2] *Pharm. Weekblad*, 1927, 64, 338.

natural camphor, but shows no optical rotation. "Turpentine camphor" consists of pinene hydrochloride. M.Pt. 125° C.

Determination.—The following method[1] gives satisfactory results for the determination of camphor in pills and tablets. Take a sufficient quantity of the powdered substance to contain about 2 gm. of camphor, and place in a 400 cc. round-bottomed flask with 10 cc. of benzene and 10 cc. of water. Steam distil with an efficient condenser into a 200 cc. flask until about 100 cc. have been collected. Wash out the condenser with 5 cc. of alcohol, followed by 10 cc. of benzene. Saturate the distillate with sodium chloride, and acidify with dilute sulphuric acid. Transfer to a separator, and draw off the aqueous layer into a second separator. Rinse the receiver with 10 cc. of benzene into the second separator. Shake, separate, and extract once more with 10 cc. of benzene. Shake the combined benzene extracts with 10 cc. of aqueous salt solution made alkaline with sodium carbonate. Separate, and shake the washings with 10 cc. of benzene. Make up the benzene solution to 50 cc. in a graduated flask, filter into a 200 mm. polarimeter tube, and take the reading at 20° C. $C=2{\cdot}4683\frac{a}{L}-0{\cdot}01747\frac{a^2}{L^2}$, where a=rotation in angular degrees and L=length of tube in decimeters. $\frac{C}{2}$=number of grams of camphor present in the sample.

Camphor Monobromide (Monobromocamphor), $C_{10}H_{15}BrO$. M.W.=231·0. —Forms colourless needles or scales. M.Pt. 74° to 76° C. The ash should be inappreciable. Almost insoluble in water; solubility in alcohol, 15 at 25° C.; soluble in ether.

Tests.—On shaking 0·5 gm. with 10 cc. of water and filtering, the filtrate should not become more than slightly opalescent with silver nitrate, but on boiling with silver nitrate solution it should be decomposed with precipitation of silver bromide.[2]

Cantharidin, $C_{10}H_{12}O_4$. M.W.=196·1.—Forms colourless crystals. M.Pt. 210° to 212° C. (B.P.), but pure samples melt up to 218° C. A 0·1 per cent. solution in almond oil or chloroform blisters the skin. Very slightly soluble in alcohol; solubility in chloroform, 1·5; in acetone, 2·5; in ether, 0·15; in almond oil, 0·1. For determination, see Cantharides (p. 224).

Carbon Disulphide, CS_2. M.W.=76·1.—A colourless, mobile, highly refractive liquid having a characteristic and unpleasant odour. The odour of the impure varieties is highly offensive. It is an excellent solvent for phosphorus, sulphur, and iodine. B.Pt. 46·5° C.; S.G. 1·269 to 1·270. It should be practically free from non-volatile residue (less than 0·005 per cent.). Almost insoluble in water, readily miscible with alcohol, ether, or chloroform. On shaking about 10 cc. with half its volume of water the latter should not be acid to litmus.

Carbon Tetrachloride (Tetrachlormethane), CCl_4. M.W.=153·8.—A colourless, heavy liquid, having a pleasant but somewhat suffocating odour. Slightly soluble in water, 0·1; miscible with alcohol or ether. B.Pt. (pure), 76·7° C.; S.G. 1·6037.

[1] Eaton, *J. Ass. Off. Agric. Chem.*, 1926, **9**, 289.

[2] For the estimation of the monobromocamphor in tablets, see Methods of Analysis, *Ass. Off. Agric. Chem.*, 1925, 393.

Tests.—It should be free from non-volatile residue. On shaking with water the aqueous layer should not become acid to litmus, and should not contain chlorine or chlorides. It should not become coloured on shaking for some time with conc. sulphuric acid, neither should any reducing action take place on the addition of a little potassium chromate.

Sulphur Compounds.[1]—To 10 cc. of the sample add 3 cc. of alkaline plumbite solution and 1 cc. of absolute alcohol. Boil and shake for a few minutes, allow to stand. Not more than a faint brown coloration should be formed in the upper layer. The alkaline plumbite solution is made by dissolving 0·5 gm. of lead acetate in 20 cc. of water, and then adding 20 gm. of pure caustic potash.

Carbon Disulphide may be tested for by mixing 10 cc. with an equal volume of alcoholic potash (10 per cent.), allowing to stand for some time, and then adding 5 cc. of acetic acid (33 per cent.) and a little copper sulphate solution; a yellow precipitate either immediately or on standing indicates carbon disulphide. This method has been made use of as a method of determination.[2]

Determination of Carbon Disulphide.—Dissolve 1·5 gm. of potassium hydroxide in 5 cc. of water. When cold add 5 cc. of absolute alcohol and 5 cc. of the sample. Shake, heat to boiling, cool, dilute with water to 200 cc., neutralise to phenolphthalein with acetic acid. Add 2 gm. of sodium bicarbonate, and titrate with *N*/100 iodine. 1 cc. *N*/100 iodine ≡ 0·00076 gm. CS_2. Carry out a blank experiment without the sample, and subtract the value obtained.

Chloral Formamide, $C_3H_4Cl_3NO_2$. M.W.=192·4. — Forms colourless, odourless, lustrous crystals, having a somewhat bitter taste. M.Pt. 114·5° C. The aqueous and alcoholic solutions should be neutral. On careful ignition no residue should be obtained and no inflammable vapours should be given off. Solubility in water, 5; in alcohol, about 65; very soluble in ether; slowly soluble in glycerine (=8).

Tests.—No immediate turbidity should be produced on adding a little silver nitrate to a 10 per cent. alcoholic solution. It is hydrolysed in aqueous solution if heated much above 50° C.; is not affected by weak acids, but it is decomposed by dilute alkalis into chloroform, ammonia, and sodium formate. This may be used as a method of determination.

Chloral Hydrate, $CCl_3.CHO.H_2O$. M.W.=165·4.—Colourless, monoclinic, non-deliquescent crystals. M.Pt. 49° to 53° C., but begins to soften earlier. It should completely volatilise on heating. The alcoholic solution (10 per cent.) should be neutral, and should not be affected by silver nitrate solution. Solubility in water, 330; in alcohol, 160; in ether, 270; in chloroform, 30.

Determination.—Dissolve 6 gm. in 50 cc. of *N* sodium hydroxide, and after two minutes titrate back with *N* hydrochloric acid to phenolphthalein. 1 cc. *N* NaOH ≡ 0·01654 gm. $CCl_3.CHO.H_2O$.[3]

Tests.—The B.P. requires that a solution in chloroform shaken with sulphuric acid shall not impart any colour to the acid, but E. Merck[4]

[1] Perkins, *Y.B.P.*, 1924, 629.
[2] Radcliffe, *J. Soc. Chem. Ind.*, 1901, **28**, 229.
[3] For other methods of determination, see *Pharm. J.*, 1906, **76**, 162; 1907, **79**, 4; *J. Soc. Chem. Ind.*, 1903, **22**, 1019; Kolthoff, *Pharm. Weekblad*, 1923, **60**, 2.
[4] *Annual Reports*, 1910, **24**, 140.

suggests the following: If 2 gm. of chloral hydrate are dissolved in 10 cc. of sulphuric acid (S.G. 1·84) and 4 drops of formaldehyde (40 per cent.) are added, no colour should appear within half an hour; a glass-stoppered bottle is used, previously rinsed out with sulphuric acid. The B.P. also requires that "when 1 gm. of chloral hydrate is warmed with 6 millilitres of water and 0·5 millilitres of solution of sodium hydroxide (20 per cent.), the mixture filtered, sufficient *N*/10 solution of iodine added to impart a deep brown colour, and the whole set aside for an hour, no yellow, crystalline precipitate shall be produced (absence of chloral alcoholate)."

Chloralose (Glucochloral; α-Chloralose), $C_8H_{11}O_6Cl_3$. M.W.=309·5.—Fine, colourless crystals, slightly soluble in water, 0·6; very soluble in hot water, alcohol, or ether. M.Pt. 185° C. It should be free from β-chloralose, which is insoluble in cold water, and has M.Pt. 229° C.

Chloramine-T (*p*-Toluene sodium sulphochloramide), $CH_3.C_6H_4SO_2.N.NaCl.3H_2O$. M.W.=281·6.—A white powder or laminæ having a faint, chlorine-like odour. Solubility in water, 15. Contains 12·58 per cent. of chlorine.

Determination of Active Chlorine.—Dissolve 1 gm. in hydrochloric acid, and titrate the liberated iodine with *N*/10 thiosulphate in the usual manner. 1 cc. *N*/10 $Na_2S_2O_3 \equiv 0{\cdot}02816$ gm. Chloramine-T. The chlorine should be between 12·35 and 12·58 per cent.

Dichloramine-T, or *p*-Toluenesulphodichloramide, $CH_3C_6H_4SO_2.NCl_2$, is a similar compound for use in oily solutions.

Chlorbutol (*Chloretone*, Trichlorbutyl alcohol), $CCl_3(CH_3)_2.COH$. M.W= 177·4.—Small, white, crystalline flakes, or large, transparent crystals, with characteristic camphoraceous odour, slightly soluble in water, 0·8, readily soluble in most other solvents. M.Pt. 96° C. when anhydrous, but the compound is usually somewhat hydrated, and melts at 80° to 81° C. B.Pt. 167° C. Chlorbutol gives the iodoform reaction, and on warming with aniline and potassium hydroxide, phenyl *iso*cyanide is formed.

Chloroform, $CHCl_3$. M.W.=119·4.—A heavy, colourless, volatile liquid, with a characteristic sweetish odour. Chloroform (B.P.) contains 2 per cent. absolute alcohol; chloroform (U.S.P.) 0·5 to 1 per cent. alcohol. S.G. 1·498 when pure; B.P. 1·483 to 1·487; U.S.P. 1·474 to 1·478 at 25° C.; B.Pt. (pure) 61·2° C. Slightly soluble in water, 0·5; miscible in all proportions with alcohol or ether.

Tests.—Anæsthetic or B.P. chloroform should comply with the following tests: It should boil almost entirely between 59·5° and 61·5° C. On collecting the last 10 per cent. of the distillate and allowing it to evaporate spontaneously on filter paper no odour other than that of alcohol and chloroform should result. No appreciable residue should result on evaporating 20 cc.

Organic Impurities.—When 20 cc. are mixed with 15 cc. of conc. sulphuric acid, no visible coloration should be imparted after the addition of 0·4 cc. of pure 40 per cent. formaldehyde solution and shaking for five minutes.

Acetaldehyde.—5 cc. shaken with 5 cc. of Schiff's reagent (decolorised fuchsin) should give no purple colour after fifteen minutes. On shaking about 5 cc. with twice its volume of water the aqueous layer should not be acid to methyl red nor give a turbidity with silver nitrate solution, nor a colour with cadmium potassium iodide and starch solutions. When

20 cc. are shaken for twenty-five minutes with 15 cc. of conc. sulphuric acid and 2 cc. of the acid are diluted with 5 cc. of water, the liquid should remain colourless and clear, and should possess no foreign odour. The liquid, diluted further with 10 cc. of water, should remain clear, and give no precipitate with silver nitrate solution.[1]

Cinchonidine, $C_{19}H_{22}ON_2$. M.W.=294·2.—Forms white crystals. M.Pt. 202° C. Solubility in alcohol, 6; in ether, 0·53; readily soluble in chloroform.

Tests.—A 0·1 per cent. solution in dilute sulphuric acid shows only a faint blue fluorescence. It does not give the thalleioquin reaction (see Quinine, p. 166), and yields an insoluble compound with sodium potassium tartrate, thus distinguishing it from cinchonine and quinidine.

Cinchonidine Sulphate, $(C_{19}H_{22}N_2O)_2.H_2SO_4.7H_2O$. (B.P.C.) M.W.= 812·8.—[The $3H_2O$ salt (M.W.=740·5) is official in the U.S.P.] Cinchonidine content, 72·4 per cent.; water content, 15·5 per cent. Forms silky needles or thin prisms. The amount of water of crystallisation varies; the U.S.P. requires that the compound shall not lose more than 12 per cent. at 100° C. Slightly soluble in water (1·0). The anhydrous sulphate is almost insoluble in chloroform, resembling quinine sulphate.

Tests.—It should respond to the tests given above, under cinchonidine. A dilute solution of cinchonidine sulphate gives characteristic crystals with platinum chloride solution even at 0·005 per cent. strength.

Cinchonine, $C_{19}H_{22}ON_2$. M.W.=294·2.—Shining prisms or needles. Almost insoluble in water, slightly soluble in alcohol, 0·8; in chloroform, 0·3; in ether, 0·3; more soluble in amyl alcohol, 1·0; but the solubility varies with the condition of the alkaloid.

Tests.—Cinchonine solutions in sulphuric acid are not fluorescent, and do not give the thalleioquin test. Cinchonine salts do not give a precipitate with sodium potassium tartrate (distinction from quinine and cinchonidine). Cinchonine is also distinguished from quinine by its slight solubility in ether. Commercial cinchonine and its salts often contain a considerable proportion of hydrocinchonine, which renders them more soluble.

Cinchonine Hydrochloride, $C_{19}H_{22}ON_2.HCl.2H_2O$. M.W.=366·7. (Cinchonine, 80·2 per cent.; water, 9·6 per cent.)—White crystals. Readily soluble in water and alcohol; slightly soluble in ether and chloroform.

Tests.—When heated in a dry test-tube purple fumes are evolved. A 0·1 per cent. solution gives on the careful addition of sodium carbonate solution characteristic crystals which under the microscope are seen to be in the form of small rosettes. For other tests, see Cinchonine above.

Cinchonine Sulphate, $C_{19}H_{22}ON_2.H_2SO_4.2H_2O$. M.W.=722·5. (Cinchonine, 81·4 per cent.; water, 5·0 per cent.)—Forms white, shining crystals. Solubility in water, 1·7; in alcohol, 10; insoluble in ether. The anhydrous salt is soluble in 22 parts of boiling chloroform.

Tests.—See under Cinchonine and Cinchonine Hydrochloride above.

Citric Acid, $CH_2COOH.C(OH)COOH.CH_2.COOH.H_2O$. M.W.=210·1.—Large transparent prisms. Solubility in water, 160; in alcohol, 100 (at 25° C.); in ether, 2·3.

Determination.—Titrate 1·5 gm. with $N/2$ NaOH to thymol blue to a blue colour. 1 cc. $N/2$ NaOH $\equiv$ 0·03501 gm. $H_3C_6H_5O_7.H_2O$.

[1] For the determination of chloroform in drug products, see Moraw, *J. Ass. Off. Agric. Chem.*, 1925, **8**, 526.

Tests.—The residue on ignition should not exceed 0·05 per cent. The B.P. test for tartaric acid is that 1 gm. of the powdered acid mixed with 10 cc. of sulphuric acid acquires not more than a pale yellow colour when kept at a temperature of 80° C. for an hour. A more delicate test is as follows: 1 gm. dissolved in 5 cc. of a 33 per cent. clear solution of potassium acetate should not give any turbidity on standing for thirty minutes after the addition of an equal volume of alcohol. The B.P. limit for lead is 20 parts per million, making alkaline with ammonia before testing (2 gm. of citric acid require about 7 cc. of 10 per cent. ammonia).

Arsenic.—Limit, 1·4 parts per million, the test being carried out by the general method. Citric acid should be free from sulphate. Oxalate may be tested for by making the aqueous solution alkaline with ammonia and adding calcium chloride solution.

Cocaine, $C_{17}H_{21}O_4N$. M.W.=303·2.—Forms large, colourless crystals or a white, crystalline powder. M.Pt. 98° C. Solubility in water, 0·14; in alcohol, 20; in ether, 26; very soluble in chloroform.

Tests.—For carrying out the following tests cocaine is converted into the hydrochloride by dissolving 0·2 gm. in alcohol, neutralising with *N*/2 HCl to methyl red and evaporating to dryness.

Permanganate Test.—0·01 gm. dissolved in 1 cc. of half-saturated alum solution yields, on adding to a drop of saturated potassium permanganate solution which has been allowed to dry on an object-glass, a violet, crystalline precipitate which shows characteristic aggregates under the microscope.[1] No reduction of the permanganate should occur (absence of cinnamyl cocaine). The most sensitive reaction for cocaine is the crystalline precipitate formed with gold chloride. The crystals show characteristic forms under the microscope.

Maclagan's Test.—0·1 gm. is dissolved in 100 cc. of water and 0·25 cc. of 10 per cent. ammonia stirred in. The sides of the beaker are rubbed occasionally, but not too vigorously, with a glass rod during fifteen minutes. A crystalline deposit separates, leaving the supernatant liquid clear. The formation of an amorphous turbidity shows excess of amorphous alkaloid. Cocaine may be titrated satisfactorily to methyl red. When treated by Vitali's test for atropine (p. 131), cocaine develops a peculiar, pleasant odour variously described as resembling meadowsweet, peppermint, or citronella.

Cocaine Hydrochloride, $C_{17}H_{21}O_4N.HCl$. M.W.=339·6. (Cocaine content, 89·3 per cent.)—Forms white prisms, very soluble in water (250 at 25° C.) and alcohol (38 at 25° C.). M.Pt.: when placed in a bath at 195° C., and the heating continued, pure cocaine hydrochloride melts at 200° to 202° C. Commercial specimens should not melt below 196° C. Prolonged heating reduces the M.Pt. The limits of the B.P. and other pharmacopœias are too low. $[\alpha]_D$ (in 2 per cent. aqueous solution)=+71·95°.

Tests.—Cocaine hydrochloride should answer the tests given above under Cocaine. Other salts of cocaine occasionally met with are the sulphate, nitrate, and salicylate.

Codeine, $C_{18}H_{21}NO_3.H_2O$. M.W.=317·2. (Anhydrous codeine content, 94·3 per cent.)—Forms colourless crystals, slightly soluble in water, 0·84; soluble in alcohol, 60; very soluble in chloroform, less so in ether. M.Pt. 155° to 156° C.

[1] Cf. *Analyst*, 1911, **36**, 2; 1919, **44**, 192.

Tests.—Codeine is soluble in excess of ammonia solution, but not in sodium or potassium hydroxide. 0·1 gm. dissolves in 1 cc. of cold sulphuric acid to a colourless solution, but on gently warming with a trace of ferric chloride solution a blue colour is developed, changed to red, and then to yellow by a drop of dilute nitric acid. Morphine may be detected by the fact that codeine gives no blue colour, but only a dull green, on the addition of dilute ferric chloride solution and very dilute potassium ferricyanide solution to a solution made acid with hydrochloric acid. Dilute solutions of codeine (1 : 200)give with Marme's reagent (see Appendix) characteristic crystals consisting of masses of rods, which may be readily distinguished microscopically from those given by morphine with the same reagent.

Codeine Hydrochloride, $C_{18}H_{21}NO_3.HCl.2H_2O$. M.W.=371·7. (Anhydrous codeine, 80·5 per cent.; water, 9·7 per cent.)—White crystals, soluble in water, 5. May be tested as under Codeine above.

Codeine Phosphate, $C_{18}H_{21}NO_3.H_3PO_4.2H_2O$. M.W.=433·3. (Anhydrous codeine, 69·0 per cent.; water, 8·3 per cent.)—White, efflorescent crystals, soluble in water, 45; only slightly soluble in alcohol or chloroform. Codeine phosphate gives the tests given under Codeine and the tests for phosphates.

Colchicine, $C_{22}H_{25}NO_6$. M.W.=399·2.—A yellowish-white, amorphous powder, becoming darker on exposure to light. M.Pt. with decomposition, 143° to 147° C.; 142° to 146° C. (U.S.P.). Solubility in water, 9·6; only slightly soluble in ether; very soluble in chloroform.

Tests.—A violet-blue colour changing to yellow is formed on the addition of a drop of nitric acid to a small amount of colchicine. Colchicine forms no crystalline precipitates with the ordinary reagents. The addition of 2 drops of ferric chloride solution to 5 cc. of a 1 in 100 aqueous solution of colchicine produces no colour, but on heating, a brownish-red colour is developed, changing to brownish black (absence of colchiceine).

Colchicine Salicylate.—A yellow, amorphous powder, soluble in water or alcohol. For tests, see under Colchicine. Owing to the presence of salicylate the ferric chloride test does not, of course, apply to this salt.

Coniine, $C_8H_{17}N$. M.W.=127·1.—An almost colourless liquid with an objectionable odour suggesting a foul tobacco pipe. When diluted with water, a peculiar mouse-like odour is noticeable even in high dilution. It becomes brown on exposure to the air. B.Pt. 166° C. Solubility in water, 1·8; soluble in alcohol, ether, or chloroform.

Tests.—It gives characteristic crystals with phosphotungstic acid in very dilute solutions.

Corynine (Yohimbine), $C_{22}H_{30}O_4N_2$. M.W.=386·4.—Forms white needles, becoming yellow on exposure to light. Almost insoluble in water; soluble in alcohol or chloroform; slightly soluble in ether. M.Pt. 331° to 334° C.

Tests.—Corynine becomes deep green, then yellowish, on treatment with fuming nitric acid, and on the addition of alcoholic potash to the product a cherry-red colour is produced. If corynine is dissolved in sulphuric acid and a trace of chlorinated lime added an intense orange-red colour is produced.

Corynine Hydrochloride (Yohimbine hydrochloride), $C_{22}H_{30}O_4N_2.HCl$. M.W.=422·9.—Occurs as colourless crystals, slightly soluble in water. M.Pt. 287° C.

Cotarnine, $C_{12}H_{15}O_4N$. M.W.=237·2.—Cotarnine is an oxidation product

of narcotine. Forms colourless crystals, slightly soluble in water, soluble in alcohol or ether, and in ammonia. M.Pt. 132° to 135° C.

Cotarnine Hydrochloride (*Stypticin*), $C_{12}H_{16}NO_4Cl$. M.W.=273·6.—A pale yellow, crystalline powder, readily soluble in water and alcohol. A method of determining cotarnine by precipitation as picrolonate has been suggested.[1]

Cotarnine Phthalate (*Styptol*), $(C_{12}H_{15}NO_4).C_6H_4(COOH)_2$. M.W.=640·3. —A yellow or orange, crystalline powder. M.Pt. about 110° C. Readily soluble in water.

Dextrose (Pure Glucose), $C_6H_{12}O_6$. M.W.=180·1.—A white or faintly yellowish powder, very soluble in water, 82, almost insoluble in cold alcohol, more soluble in hot alcohol. It is prepared both as the anhydrous substance and as the hydrated compound containing one molecule of water. When anhydrous, dextrose melts at about 140° C., and the $[\alpha]_D$ is +52·7°, using a 10 per cent. solution at 20° C. The solution should be previously boiled or allowed to stand twenty-four hours in order to avoid bi-rotation.

Determination.—Dextrose may be determined in the absence of other sugars by means of its optical rotation or by its copper reducing power. The latter figure is determined by means of Fehling's solution. Prepare a Gooch crucible with asbestos in the usual way, and wash with hot 20 per cent. sodium hydroxide, then with hot water until free from alkali, and ignite. Mix 25 cc. of each of the two Fehling's solutions in a 250 cc. beaker covered with a clock glass, and immerse in boiling water for six minutes. Add the sugar solution after sufficient water to make 100 cc. Then heat the beaker for twelve minutes in a *boiling* water bath. Filter the precipitated cuprous oxide immediately through the Gooch crucible, wash with 400 cc. of hot water, and then with 10 cc. of alcohol and 10 cc. of ether. Ignite the crucible within a larger crucible over a hot flame for thirty minutes. After cooling, weigh the precipitate as CuO. The amount of solution taken should give a weight of CuO between 0·15 gm. and 0·40 gm. The amount of dextrose corresponding to the weight of CuO may be obtained from the table in Appendix. Fehling's solution alone frequently gives a small amount of precipitate under these conditions, and it is therefore necessary to carry out a blank determination. An alternative volumetric method is that of Lane and Eynon.[2]

Dextrose should be free from ash.

Diamorphine Hydrochloride (Diacetylmorphine hydrochloride; *Heroin*), $C_{17}H_{17}NO(OCH_3CO)_2.HCl.H_2O$. M.W.=423·6. (Diamorphine, 87·1; water, 4·2.)—A white, crystalline powder of bitter taste, soluble in water, 50, and in 90 per cent. alcohol, 9·1. M.Pt. 231° to 232° C.

Tests.—0·1 gm. dissolved in 1 cc. of sulphuric acid by warming on a water bath, cooled, and diluted with 6 cc. of water, gives a deep blue colour on the addition of a dilute solution (0·5 per cent.) of potassium ferricyanide, to which 1 drop of ferric chloride solution has been added. This test should not give a blue colour if the heating with sulphuric acid is omitted (absence of morphine).

Digitalin.—The active principles of digitalis, with the exception of digitoxin and digitalin, are not sufficiently well characterised or easily separated to be commercial products in the form of pure chemical com-

[1] Mathes and Rammstedt, *Z. Anal. Chem.*, 1807, **46**, 565.
[2] *J. Soc. Chem. Ind.*, 1923, **42**, 10.

pounds. Consequently a number of preparations consisting of mixtures of the various glucosides in different proportions are to be found in commerce. It is most important, on account of the toxic properties of digitoxin as compared with the other glucosides, that careful distinction should be made between these various products, the nomenclature of which is very confusing.

Digitoxin.—Pure digitoxin is official in the French Codex, being known as *digitaline crystallisée*, or simply as digitalin. According to the method of crystallisation digitoxin may be anhydrous, melting at about 252° C. (crystallised from chloroform-methyl alcohol), or may be in the hydrated form (from 90 per cent. alcohol), melting at about 150° C. Digitoxin is insoluble in hot or cold water, somewhat soluble in alcohol (2·3) or ether, very soluble in chloroform. If dissolved in glacial acetic acid and poured on to the surface of concentrated sulphuric acid containing a trace of ferric chloride, a dirty brown or bluish-green band appears at the zone of contact, changing to an intense indigo blue.

Digitalin Germanicum is prepared from Digitalis seeds instead of the leaves. It consists chiefly of digitalein with some digitalin and digitonin. It is soluble in water, and practically insoluble in chloroform.

Digitalin Homolle or *Amorphous Digitalin* consists chiefly of digitalin with some digitonin. It is only slightly soluble in water, but soluble in alcohol and chloroform.

Digitalin Nativelle, also known as crystallised digitalin, consists principally of digitoxin and digitonin.

Gitalin ($C_{28}H_{48}O_{10}$) is a crystalline powder, slightly soluble in water, and easily soluble in chloroform or alcohol. It melts at 150° to 155° C.

Dimethylaniline, $C_6H_5N(CH_3)_2$. M.W.=121·1.—A colourless, oily liquid when freshly distilled, but rapidly darkens on keeping. S.G. 0·956 at 20° C.; M.Pt. 2·5° C.; B.Pt. 193° C. Nearly insoluble in water; soluble in alcohol. 10 cc. should dissolve in 50 cc. of water and 40 cc. of hydrochloric acid to a clear solution having no odour.

Determination of Aniline and Methylaniline.—To 10 gm. add 20 cc. of a 10 per cent. solution of acetic anhydride in benzene; allow to stand in a stoppered flask for thirty minutes; add 50 cc. of water, shake well, and titrate against *N* NaOH, using phenolphthalein as indicator. In the same manner titrate a blank on 20 cc. of the acetic anhydride solution. The difference between the titrations should not exceed 0·2 cc.

Dimethylglyoxime, $CH_3C : (NOH)C : (NOH)CH_3$. M.W.=116·1.—A white, crystalline powder, insoluble in water, soluble in alcohol. M.Pt. 243° C. with decomposition. No residue should be obtained on ignition.

Purity Test.—Dissolve 0·24 gm. of crystallised nickel chloride ($NiCl_2 . 6H_2O$) in 100 cc. of water; heat to boiling and add 0·25 gm. of the dimethylglyoxime dissolved in 25 cc. of 90 per cent. alcohol. Add ammonia drop by drop until alkaline; cool and filter. To the filtrate add 5 cc. of 1 per cent. solution of dimethylglyoxime in 90 per cent. alcohol, heat to boiling and cool. No red precipitate should be produced.

Emetine, $C_{30}H_{44}O_4N_2$. M.W.=498·3.—A colourless, amorphous powder, readily soluble in chloroform or ether, almost insoluble in water. It rapidly becomes yellow on exposure to light. M.Pt. 68° C. Emetine may be titrated with *N*/10 hydrochloric acid to methyl red. 1 cc. *N*/10 HCl ≡ 0·02491 gm. emetine.

Emetine Bismuth Iodide,—An odourless, orange-red powder containing

27 to 30 per cent. of emetine and 18 to 25 per cent. of bismuth. Slightly soluble in water and dilute acids, with partial decomposition. The emetine may be determined by dissolving in alkali and extracting the alkaloid with chloroform.

Emetine Hydrochloride, $C_{30}H_{44}O_4N_2.2HCl$. M.W.=569·3. (Emetine content, 87·5 per cent.)—A white or slightly yellow powder containing varying amounts of water of crystallisation. It becomes yellow on exposure to light and dissolves readily in water or alcohol. The U.S.P. gives a maximum of 19 per cent. loss on drying at 100° C.

Determination of Cephæline.—Dissolve 0·1 gm. of emetine hydrochloride in 5 cc. of water, add 3 cc. of 5 per cent. sodium hydroxide solution, and shake out with 10 cc. portions of ether until no more alkaloid is extracted. Acidulate the aqueous liquid with dilute sulphuric acid, add ammonia until alkaline, and shake with 10 cc. of ether. Evaporate off the ether and add to the residue 1 cc. of sulphuric acid containing about 0·055 gm. of molybdic acid—no purple colour is produced. Ewe has shown that this test is too delicate and that no commercial samples of emetine hydrochloride, even if not containing a material proportion of cephæline, will pass the test.

It is suggested [1] that a quantitative test should be introduced, the limit of cephæline being 3 per cent., and the details as follows: Dissolve 0·6 gm. in 30 cc. of distilled water in a separator, add 18 cc. of 5 per cent. sodium hydroxide solution, and shake out with 60 cc. portions of ether until the residue obtained by evaporating 1 cc. of the ether, dissolved in 1 drop of dilute hydrochloric acid and 1 cc. of water, no longer yields a turbidity with iodine solution. About five extractions are necessary. Make the aqueous liquid acid with dilute sulphuric acid, add ammonia until alkaline, and shake out with 60 cc. of ether; separate and evaporate the ether in a tared flask. Dry the residue and weigh as anhydrous cephæline.

Ephedrine, $C_{16}H_{15}ON$. M.W.=237·1.—Ephedrine is an alkaloid obtained from species of *Ephedra,* in which it occurs together with its isomer *pseudo*-ephedrine. Ephedrine crystallises in colourless rhombic crystals. Very soluble in water, alcohol, and chloroform; nearly insoluble in petroleum ether. M.Pt. 43° C. $[\alpha]_D^{20°}$, in water +13·75°.

Ephedrine Hydrochloride, $C_{16}H_{15}ON.HCl$.—Crystallises as prismatic needles. M.Pt. 216° C. $[\alpha]_D^{20°}$ −32·5°. Easily soluble in alcohol and water. Ephedrine oxalate is only slightly soluble in cold water.

Pseudo-**Ephedrine.**—M.Pt. 118° C. $[\alpha]_D^{20°}$, in water, +50°. It is only slightly soluble in water.[2]

Ergotamine, $C_{33}H_{35}O_5N_5$. M.W. = 581·3.—Decomposes at 140° C. $[\alpha]_D$ = −155° (in 0·6 per cent. solution in chloroform). It gives the colour reaction described under Ergotoxine.

Ergotoxine, $C_{35}H_{41}O_6N_5$. M.W.=627·3.—Ergotoxine is an alkaloid found in ergot. It is a white, amorphous powder, practically insoluble in water, soluble in alcohol and ether. M.Pt. 160° to 162° C.

Colour Test.—1 mg. dissolved in 4 cc. of glacial acetic acid and mixed with 4 cc. of a cooled mixture of equal volumes of sulphuric acid and water, slowly forms an intense blue colour.[3]

[1] *Amer. J. Pharm.*, 1919, **91,** 275.
[2] See also Chou, *J. Biol. Chem.*, 1926, **70,** 109.
[3] Evers, *Pharm. J.*, 1927, **118,** 721.

Ergotoxine Phosphate, $C_{35}H_{41}O_6N_5.H_3PO_4.H_2O$, melts at 186° to 187° C.

Ergotinine, $C_{35}H_{39}O_5N_5$. M.W.=609·3.—Formed from ergotoxine by the loss of one molecule of water. It is also a constituent of ergot, but is inactive physiologically. It melts at 229° C. and has $[\alpha]_D + 338°$. It forms a crystalline citrate and gives the colour test described under Ergotoxine.

Ethyl Acetate, $CH_3COOC_2H_5$. M.W.=88·1.—A colourless, volatile, inflammable liquid with a characteristic ethereal odour. Solubility in water, 6 (this is the value for the pure substance—commercial samples are often considerably more soluble than this); miscible in all proportions with alcohol, ether, benzene, or chloroform. (Some commercial samples do not give clear solutions with the two latter solvents owing to the presence of water.) S.G. about 0·900; B.Pt. 74° to 78° C. (when pure, 77° C.).

Determination.—The amount of true ethyl acetate may be determined by saponifying 2·5 gm. of the ester with 50 cc. of *N*/2 sodium hydroxide and titrating back with *N*/2 hydrochloric acid to thymol blue. (1 cc. *N*/2 NaOH ≡ 0·04404 gm. $CH_3COOC_2H_5$). The amount of free alcohol may be determined by distillation after saponification, taking the S.G. of the distillate; from the percentage of alcohol thus found the amount of combined alcohol determined by saponification is subtracted. (1 cc. *N*/2 NaOH ≡ 0·02305 gm. C_2H_5OH.)

Tests.—No residue should be left on evaporation. It should not immediately affect blue litmus paper. On pouring a little on to a filter paper and allowing evaporation to take place, no foreign odour should be detected at any stage of the evaporation, particularly after the smell of ethyl acetate has disappeared, showing absence of foreign esters. Shaken with an equal volume (say 20 cc.) of a saturated solution of calcium chloride, no considerable increase in volume of the latter should take place. 1 cc. of ethyl acetate practically free from water will form a clear solution with 10 cc. of benzene. On pouring a little on to sulphuric acid no coloration should be produced at the junction of the two liquids. Other esters may be examined in a similar manner to the above.

Ethyl Alcohol, C_2H_5OH. M.W.=46·1.—A colourless, neutral liquid. B.Pt. 78·4° C.; S.G. 0·7938.

Determination.—Where impurities are absent the alcohol can be determined with accuracy from the S.G., or from the Refractive Index (see Appendix tables). The determination of alcohol in tinctures, etc., is dealt with on p. 265. Commercial absolute alcohol contains upwards of 99·4 per cent. by volume, the best samples having at least 99·7 per cent. by volume. Absolute alcohol B.P. has not less than 99·4 per cent. by volume. The alcohol most used in pharmacy is rectified spirit B.P., containing 90 per cent. by volume and having S.G. 0·8337 (B.P.). Other B.P. alcohols are "70 per cent." (S.G. 0·8899), "60 per cent." (S.G. 0·9134), "45 per cent." (S.G. 0·9435), and "20 per cent." (S.G. 0·9760). All these alcohols, due account being taken of their respective strengths, should correspond to the following tests for purity of absolute alcohol.

Tests.—Alcohol should mix in all proportions with water to form a clear and bright solution free from foreign odour. No residue should be left on evaporation, and no foreign odour should be detected at any stage of the evaporation, neither should any foreign odour be observed after evaporation on filter paper. It should be neutral to litmus. 100 cc. with 2 cc. of *N*/10 silver nitrate solution, exposed for twenty-four hours to bright

light and then decanted from the black powder which has formed, undergo no further change when exposed to light with more $N/10$ silver nitrate solution (absence of more than traces of amylic alcohol and other organic impurities, B.P.); the best samples, however, will not show any darkening with silver nitrate. No darkening should immediately result on the addition of a 5 per cent. solution of sodium hydroxide or of a 10 per cent. solution of ammonia. Acetone may be tested for according to the Reynolds-Gunning reaction by adding 6 cc. of baryta water and 3 cc. of a solution of mercuric chloride to 2 cc. of alcohol, shaking for one minute, filtering, and adding ammonium sulphide to the filtrate; a darkening shows the presence of acetone. Furfural may be detected by adding 0·2 cc. of colourless aniline and 2 cc. of acetic acid to 10 cc. of alcohol—in the presence of furfural a red colour will develop on standing. Methyl alcohol may be tested for according to Vorisek [1] and may be determined according to Thorp and Holon [2] for large quantities, and for small quantities according to Simmonds [3] and Jones,[4] see Ether, below; or by means of the refractometer, see Appendix table.

Ethyl Bromide, C_2H_5Br. M.W.=109·0.—A clear, colourless, highly refractive liquid having a pleasant ethereal odour. Insoluble in water, miscible with alcohol or ether in all proportions. It is liable to decomposition, but this may be checked by the addition of alcohol, which lowers the S.G. Pure ethyl bromide has S.G. 1·473 and B.Pt. 38·5° C.—a pure product containing 1 per cent. of alcohol has S.G. 1·460 and B.Pt. 38° to 40° C. A good sample should have S.G. 1·450 to 1·460 and B.Pt. 38° to 40° C. It should respond to the tests for purity given under Ethyl Chloride.

Determination.—The proportion of ethyl bromide may be determined by saponifying 2·5 gm. with 50 cc. of $N/2$ alcoholic potash and titrating back with $N/2$ hydrochloric acid. 1 cc. $N/2$ KOH ≡ 0·0545 gm. C_2H_5Br.

Ethyl Chloride, C_2H_5Cl. M.W.=64·5.—At ordinary temperatures ethyl chloride is a gas, but it is usually supplied in tubes under pressure as a colourless, mobile, and extremely volatile liquid, having a pleasant odour. Only slightly soluble in water, but miscible in all proportions with alcohol and ether. S.G. at 0° C., 0·921 (B.P. gives 0·920 to 0·960); B.Pt. 12·5° C.

Determination.—The proportion of ethyl chloride may be determined by saponifying 1·5 gm. with 50 cc. of $N/2$ alcoholic potassium hydroxide and titrating back with $N/2$ hydrochloric acid. 1 cc. $N/2$ KOH ≡ 0·03225 gm. C_2H_5Cl.

Tests.—Ethyl chloride should leave no residue on evaporation nor should any foreign odour be noticed at any stage of the evaporation. Water which has been shaken with twice its volume of ethyl chloride should be neutral to litmus and should not give a turbidity with silver nitrate. Ethyl chloride should not be coloured yellow when shaken in a stoppered cylinder (previously rinsed with sulphuric acid) with twice its volume of sulphuric acid, and the sulphuric acid on separation and dilution with water should not give a turbidity with silver nitrate nor should it have an unpleasant odour.

Ethylene Glycol, $CH_2OH.CH_2OH$. M.W.=60·1.—A colourless, practically odourless, hygroscopic liquid, miscible with water or alcohol. S.G. 1·116; B.Pt. 197° to 197·5° C. (110° C. at 30 mm. pressure).

Ethyl Ether, $(C_2H_5)_2O$. M.W.=74·1.—A colourless, mobile, highly in-

[1] *J. Soc. Chem. Ind.*, 1909, **28**, 823.
[2] *J. Soc. Chem. Ind.*, 1904, **85**, 1.
[3] *Analyst*, 1912, **37**, 16.
[4] *Analyst*, 1915, **40**, 218.

flammable liquid with a characteristic odour. Soluble in ten times its volume of water, miscible in all proportions with alcohol, chloroform, etc. B.Pt. (pure) 35° C.; S.G. 0·720, (pure) 0·7198. Commercial ether, however, always contains varying quantities of water and alcohol, and if prepared from methylated spirits may contain methyl ether. It is sold according to the S.G. Ether for medicinal use should answer to the following tests.

The *boiling-point* varies according to the grade of ether, since, if made from methylated spirits, ether will contain methyl ether and methyl ethyl ether, which will lower the B.Pt., but as water and alcohol have opposite effects this test is practically of no value.

Residue.—20 cc. spontaneously evaporated in a glass dish should leave a small quantity of moisture, having no smell, which does not redden or bleach blue litmus paper, and on evaporation leaves no residue. A quantity of ether allowed to evaporate from blotting-paper should leave no objectionable odour.

Water.—It should form a clear liquid when mixed with an equal volume of carbon disulphide (absence of excess of water).

Peroxides may be tested for by shaking 10 cc. with 2 cc. of a 10 per cent. cadmium potassium iodide solution and keeping for one hour in the dark, when no yellow colour should be produced.[1]

Acetone is often present in ether made from methylated spirit, but should not be present in ether made from rectified spirit; it may be tested for on 10 cc. of ether by adding 1 cc. of freshly made 5 per cent. solution of sodium nitroprusside and about 3 cc. of strong ammonia when, in the presence of acetone, a magenta colour develops.[2]

Aldehydes[3] may be tested for by treating with decolorised fuchsine solution. The reagent is made by adding 3 cc. of concentrated sulphuric acid to 30 cc. of 0·1 per cent. solution of fuchsine, with sufficient sulphur dioxide to saturate the liquid. Ether and this reagent are mixed in equal proportions with sufficient aldehyde-free alcohol to render the two liquids miscible. The test is not satisfactory in the presence of peroxides. The B.P. test for aldehyde consists in keeping the ether in contact with small fragments of potassium hydroxide for an hour, when no yellow coloration should be developed.

Alcohol may be determined by the method of Squibb.[4]

Methyl Compounds.—The B.P. requires that purified ether shall respond to the following test for methyl compounds: Well shake 2 volumes of the purified ether in a separating funnel with 1 volume of pure rectified alcohol (20 per cent.) and 1 volume of water; allow the mixture to separate and draw off the lower layer. Mix 5 cc. of this lower layer in a wide test-tube with 2·5 cc. of an aqueous solution (1 in 50) of potassium permanganate and 0·2 cc. of sulphuric acid. At the end of three minutes add to the contents of the tube 0·5 cc. of an aqueous solution (9·6 in 100) of oxalic acid, followed by 1 cc. of sulphuric acid, and then by 5 cc. of decolorised solution of fuchsin.[5] Mix thoroughly and set aside for twenty minutes. No violet colour is produced (absence of methyl compounds).

Ethyl Hydrocupreine Hydrochloride, $C_{21}H_{28}O_2N_2.HCl$. M.W.=376·8.—A

[1] Baskerville and Hamor, *J. Ind. Eng. Chem.*, 1911, **3**, 378.
[2] Finnemore, *Y.B.P.*, 1914, 380.
[3] See also Phelps and Rowe, *J. Amer. Chem. Soc.*, 1926, **48**, 1049.
[4] *Pharm. J.*, 1884, **15**, 74.
[5] See also Dott, *C. & D.*, 1924, **100**, 10.

white, crystalline powder, soluble in water and alcohol. M.Pt. 242° C. The base, ethyl hydrocupreine, is insoluble in water and melts at 124° C.

Ethyl Iodide, C_2H_5I. M.W.=156 0.—A colourless, ethereal liquid, almost insoluble in water, but miscible with alcohol and ether. B.Pt. 72° C.; S.G. 1·943. It may be determined by the process and should respond to the tests given under Ethyl Chloride. 1 cc. $N/2$ KOH ≡ 0·078 gm. C_2H_5I.

Ethylmorphine Hydrochloride (*Dionin*), $C_{19}H_{24}NO_3Cl.H_2O$. M.W.= 367·7. (Ethylmorphine, 85·2; water, 4·9.)—A white, odourless, crystalline powder, soluble in water, 8·7; in alcohol, 3·8. M.Pt. about 124° C. It is distinguished from morphine by giving no immediate blue colour with the ferricyanide test (see p. 158).

Eucalyptol (Cineol), $C_{10}H_{18}O$. M.W.=154·1.—Eucalyptol is the chief constituent of medicinal eucalyptus oil. It is a colourless or pale yellow liquid, with a strong camphoraceous odour, miscible in all proportions with alcohol, ether, or chloroform. It has the following characteristics: S.G. 0·928 to 0·930; refractive index, 20° C., 1·4590; optical rotation, nil; boiling range, 176° to 177° C.; freezing-point, not below 0° C. The cineol may be determined as under Eucalyptus Oil (see p. 316).

Eugenol, $C_{10}H_{12}O_2$. M.W.=164·1.—Eugenol is the chief constituent of clove oil. It is a colourless or slightly yellow liquid, soluble in all proportions of alcohol. S.G. 1·070; refractive index, 20° C., 1·5439; B.Pt. 253° C.; optical rotation, nil. Eugenol may be determined by absorption with sodium hydroxide (see method for Phenols, p. 310). Ferric chloride produces a blue colour on adding to the alcoholic solution.

Formaldehyde, H.CHO. M.W.=30·0.—Pure formaldehyde is a gas at ordinary temperatures. B.Pt. −21° C. It is placed upon the market in the form of an aqueous solution, containing nominally 40 per cent. of formaldehyde with more or less methyl alcohol. The B.P. requires not less than 36 nor more than 38 gm. of formaldehyde per 100 cc. of solution. The solution is a colourless liquid having a pungent and characteristic odour. The B.P. requires S.G. 1·079 to 1·081, but this will depend both on the content of formaldehyde and also on that of methyl alcohol. On evaporation, polymerisation takes place with formation of *paraform* (*q.v.*), a white, amorphous powder, which should leave no residue on ignition.

Determination.—Formaldehyde may be determined by diluting 5 cc. to a litre and taking 10 cc. of the diluted solution, adding 25 cc. of $N/10$ iodine solution and 2 cc. of 10 per cent. sodium hydroxide solution, and titrating the unused iodine with $N/10$ sodium thiosulphate solution. 1 cc $N/10$ I ≡ 0·001501 gm. H.CHO. This process is not accurate in the presence of acetone or ethyl alcohol (a positive iodoform reaction), and in such a case the hydrogen peroxide method of the B.P. may be used.

Tests.—Formaldehyde should not be more than slightly acid to litmus, and on dilution with water no reaction should be obtained with hydrogen sulphide, barium chloride, or silver nitrate. Acetone may be tested for by adding about 10 cc. of $N/10$ iodine solution to 1 cc. of formaldehyde and almost decolorising with sodium hydroxide solution; no precipitate or odour of iodoform should be produced. Methyl alcohol may be determined by the method of Lockemann and Cromer,[1] who also give a method for formaldehyde. No colour should develop on mixing with an equal volume of N sodium hydroxide solution and allowing to stand.

[1] *Z. Anal. Chem.*, 1915, **54**, 11; *Analyst*, 1915, **40**, 237.

Paraform.—A polymerised formaldehyde known as paraform is an articl of commerce. It is a colourless, amorphous substance, soluble in warı water, but insoluble in cold water. It may be determined by dissolvin 0·5 gm. of the powdered paraform in 20 to 25 cc. of *N* sodium hydroxid solution, diluting to 50 cc., and proceeding as for solution of formalin.

Formamol (Hexamethylenetetramine anhydromethylene citrate).—Thi substance contains about 40·7 per cent. of hexamine, and is also know as *Helmitol* or *Neurotropine*. It is a white, crystalline powder, soluble i water (about 20), slightly soluble in alcohol. Decomposes at 165° t 175° C. On heating with dilute acids formaldehyde is liberated.

Formic Acid, H.COOH. M.W.=46·0.—A colourless, mobile, hygroscopi liquid, having an irritating smell. Miscible in all proportions with alcohc and water. S.G. 1·225; B.Pt. 101° C.

Determination.—It may be determined by titration with sodiun hydroxide solution to phenol red. 1 cc. *N*/2 NaOH ≡ 0·02301 gm. H.COOH Or a 1 per cent. solution made alkaline with sodium carbonate may b heated with a known excess of *N*/10 potassium permanganate solution fo half an hour on the water bath, cooled, and acidified with sulphuric acid potassium iodide added, and the liberated iodine titrated with *N*/10 thio sulphate solution. 1 cc. *N*/10 $KMnO_4$ ≡ 0·002301 gm. H.COOH. A ı per cent. solution should not give a reaction for chlorides, and when neutral ised with ammonia should not give reactions for heavy metals or for oxalates No objectionable odour should be observed on treatment with excess o sodium hydroxide (absence of empyreumatic matter). The following tes is proposed for acetic acid (Hessner): "If 1 cc. of formic acid is warmed oı the water bath with 20 cc. of water and 6 gm. of yellow mercuric oxide, anı frequently shaken until no further evolution of gas takes place, on filtering the filtrate should not be acid." No residue should be left on evaporation The acid should be free from sulphates.

Gallic Acid, $C_6H_2(OH)_3.COOH.H_2O$. M.W.=188·1.—A colourless o pale yellow, crystalline powder, having no odour and an astringent acıı taste. M.Pt. 220° C. (with decomposition). Solubility in water, 1; iı alcohol, 23; in ether, 2·5.

Tests.—It may be determined by the method of Dreaper.[1] No residuı should be left on ignition—sulphates should be absent. The aqueous solutioı should not give a precipitate with a solution of gelatin (absence of tannic acid) On drying at 100° C. the water of crystallisation (9·58 per cent.) is given off.

Gelsemine Hydrochloride, $C_{20}H_{22}N_2O_2.HCl$. M.W.=358·6.—A white crystalline powder, soluble in water. The alkaloid obtained from it is crystal line and melts at 178° C. It must be distinguished from gelsemine and it salts, which are amorphous and intensely toxic. A small crystal of gelse mine treated with a drop of conc. sulphuric acid and a trace of powdereı potassium dichromate gives a fine reddish-purple colour. Gelsemine give characteristic crystalline precipitates with gold and platinum chlorides.

Glucose.—Glucose occurs in pharmacy as purified dextrose, botl anhydrous and hydrated (see p. 142), and in the commercial form as solic or lump glucose and as glucose syrup, both of which consist essentiall of a mixture of dextrin, maltose, and dextrose in varying proportions.

Glucose, Commercial.—Solid glucose is found as pale yellow lumpı containing about 12 per cent. of water. Glucose syrup is a colourless

[1] *J. Soc. Chem. Ind.*, 1893, **12**, 412.

sticky syrup, containing not more than about 20 per cent. of water. Both varieties consist of dextrin, maltose, dextrose, and unfermentable matter. Usually a small amount of ash is found, consisting chiefly of calcium sulphate; a good syrup should not contain more than 0·5 per cent. Glucose is usually prepared by the hydrolysis of starch with sulphuric acid, the acid afterwards being removed as calcium sulphate, of which a small amount remains in solution. The presence of calcium sulphate is sometimes an indication of the presence of glucose in syrups which it may be used to adulterate, *e.g.* in honey or golden syrup.

Arsenic.—Dissolve 5 gm. in 50 cc. of water, add 0·5 cc. of bromine and 10 cc. of hydrochloric acid. After allowing to stand for fifteen minutes in a warm place, remove the bromine by the addition of stannous chloride solution, and proceed as usual. The B.P. limit is 2 parts per million.

Sulphite.—Dissolve 10 gm. in 100 cc. of water and add 10 cc. of *N*/10 iodine. After shaking, titrate the solution immediately with *N*/10 thiosulphate. Not less than 6·8 cc. should be required (B.P.)[1] See also Gelatine (p. 231).

Composition.—An approximate determination of dextrose and maltose (neglecting dextrin) may be obtained by determining the copper reducing power and the optical rotation, but a more accurate determination may be made as follows: Let the weight of CuO from 1 gm. glucose be C_1 and the $[\alpha]_D$ be A_1. 250 cc. of a 10 per cent. solution, after previous boiling, are fermented with 1 gm. of washed and pressed yeast for seventy-two hours at 26° C. The liquid is boiled for twenty minutes to remove alcohol, made up to 250 cc., filtered, and the rotation and reducing power again determined (A_2 and C_2). At the same time another 250 cc. of 10 per cent. solution are treated with malt diastase and yeast simultaneously under the same conditions, and the rotation and reducing power again determined (A_3 and C_3). These figures are due to unfermentable matter. C_2—C_3 calculated to maltose gives the maltose as maltodextrin. A_2—A_3—$[\alpha]_D$ due to maltose as maltodextrin$=[\alpha]_D$ due to dextrin (A_D), whence the dextrin may be calculated, ($[\alpha]_D=200°$). The maltose and dextrose may be calculated as follows: Percentage maltose$=(A_1-A_3-A_D)\times0{\cdot}9496-(C_1-C_3)\times22{\cdot}69$; percentage dextrose$=(C_1-C_3)\times59{\cdot}43-(A_1-A_3-A_D)\times0{\cdot}589$.

Glycerin, $C_3H_5(OH)_3$. M.W.=92·0.—A colourless, viscid, hygroscopic liquid, having a sweet taste. Miscible with water or alcohol in all proportions; insoluble in ether, chloroform, petroleum, or benzene. The B.Pt. of anhydrous glycerin is 290° C. Commercially pure glycerin is sold in three strengths indicated by 1·24 S.G., 1·25 S.G., and 1·26 S.G.; the latter is the strength adopted by the B.P.

Determination.—The strength may be determined from the S.G., or from the Refractive Index (see Appendix tables). It may be determined chemically by the triacetin method (Lewkowitsch) as follows: Heat 1·5 gm. of glycerin to boiling with 8 to 10 cc. of acetic anhydride and 4 gm. of sodium acetate in a round-bottomed flask of about 100 cc. capacity under a reflux condenser for one and a half hours. Allow to cool a little, rinse out the condenser with hot water, and bring the acetic anhydride into solution by gentle agitation.

[1] This method is only approximate. For exact methods, see *Analyst*, 1927, **52**, 352 and 1928, **53**, 118. The permissible amount under the Public Health (Preservatives, etc. in Food) Regulations is 450 parts of sulphur dioxide per million.

If necessary, the contents of the flask may be gently heated, but must not be boiled, as triacetin is volatile with steam. Filter the liquid from the flocculent precipitate which separates into a wide-necked flask of about 500 to 600 cc. capacity, and allow to cool to the ordinary temperature. Add phenolphthalein and neutralise the acetic acid with sodium hydroxide solution of about 5 per cent. strength. During the addition of the alkali the flask must be continually shaken round in order to prevent any local excess of alkali. The neutral point is reached when the pale yellow colour just becomes reddish-yellow. The addition of so much alkali that a red colour is formed must be avoided; if any excess has been accidentally added, so that the neutral point has been overstepped, the determination must be repeated. With practice the colour change can be easily observed. Then add exactly 25 cc. of sodium hydroxide solution of about 10 per cent. strength, the strength of this solution being determined by a blank experiment, and boil the solution for a quarter of an hour. Titrate back the free alkali in both experiments with *N* hydrochloric acid—that is, the total alkali in the blank experiment, and the excess of alkali in the experiment proper. The difference gives the amount of alkali required for the saponification of the triacetin. Glycerin may also be determined by Hehner's modification of the dichromate method. Lewkowitsch has shown, however, that this latter method gives results too high, except when the glycerin is absolutely pure. The method is very suitable for determining pure glycerol in aqueous solutions. For a full description of this and other methods for the examination of glycerin the report of the International Committee on Glycerin Analysis[1] should be consulted.

Tests.—The ash should not be more than about 0·01 per cent., while the residue obtained by heating in an oven in a platinum dish to 160° C. (polyglycerols) should not be more than 0·03 per cent.[2] A 10 per cent. aqueous solution should be neutral to litmus, and should not give any reactions for ammonia, chlorides, sulphates, oxalates, or heavy metals, neither should it have any action upon ammoniacal silver nitrate. Only the faintest coloration should be produced on treating with an equal volume of concentrated sulphuric acid, the liquid being kept cool. No fruity odour should be produced on warming a mixture of 10 cc. of glycerin, 5 cc. of alcohol, and 5 cc. of 10 per cent. sulphuric acid, showing absence of volatile fatty acids. 5 gm. of glycerol treated with sodium hydroxide as a blank in the Reichert process (p. 287) should not require more than 0·5 cc.[3] of *N*/10 sodium hydroxide. Glycerin should not reduce Fehling solution either before or after "inversion."

Glycerophosphoric Acid, $C_3H_5(OH)_2O.PO(OH)_2$. M.W.=172·1.—This substance is not known in the pure condition, but is found in commerce in solutions of 50, 25, or 20 per cent. strength. It should be colourless and odourless.

Determination.—Titrate 1 gm. with *N*/2 sodium hydroxide to thymol blue until a definite blue colour is formed. 1 cc. *N*/2 NaOH ≡ 0·043 gm. $C_3H_9O_6P$.

Tests.—When 1 drop is warmed with 5 cc. of dilute nitric acid and 5 cc. of ammonium molybdate solution, no immediate precipitate should be formed. For the determination of phosphoric acid, see p. 90. Other common impurities are calcium, iron, and sulphate.

[1] *Analyst*, 1911, **36**, 319. [2] *Cf.* Grimwood, *J. Soc. Chem. Ind.*, 1913, **32**, 1039.
[3] The best samples require not more than 0·2 cc.

Arsenic.—By the general method on 2 gm. Limit, 5 parts per million.

Lead.—By the general method on 7 gm. with 2 gm. in the control. Limit, 10 parts per million. Should phosphate and calcium be present the lead may be difficult to determine on account of precipitation on making alkaline. In this case the lead may be determined as under Calcium Phosphate (p. 62). For salts, see Part II., Section 2.

Guaiacol, $C_6H_4\langle^{OH\ (1)}_{OCH_3\ (2)}$. M.W.=124·1.—A clear, colourless, oily liquid, with B.Pt. 205° C. and S.G. 1·118 to 1·120, or colourless crystals, M.Pt. 28° C. Optically inactive; should leave no residue on evaporation. Solubility in water, 1·3; freely soluble in alcohol, ether, glycerin, or fixed oils. It should dissolve in twice its volume of 15 per cent. potassium hydroxide to form a colourless solution setting to an almost white mass on cooling; the white mass should be soluble in 10 volumes of water.

Tests.—On shaking with twice its volume of petroleum ether, and being allowed to stand, two clear layers should be formed. No coloration should be produced with concentrated sulphuric acid.

Guaiacol Carbonate, $(C_6H_4.OCH_3.O)_2CO$. M.W.=274·1.—A white, odourless, crystalline powder. M.Pt. 86° to 88° C. (85° to 88° C., B.P.). Insoluble in water; solubility in alcohol, 2; in ether, 7·5.

Tests.—No residue should be obtained on ignition. No coloration should be produced with concentrated sulphuric acid. The alcoholic solution treated with a dilute solution of ferric chloride should not assume a green colour (absence of free guaiacol)—the alcoholic solution should be neutral to litmus. The filtered aqueous extract should not contain chlorides.

Guanidine Carbonate, $[(NH_2)_2.C.NH_2]_2.H_2CO_3$. M.W.=180·1.—A white, crystalline powder, soluble in water, forming a clear, colourless solution. Common impurities are chloride and sulphate.

Determination.—About 5 gm. dissolved in water may be titrated with *N* sulphuric acid to bromocresol green. 1 cc. *N* $H_2SO_4 \equiv 0{\cdot}09007$ gm. $[(NH_2)_2.C.NH_2]_2.H_2CO_3$.

Hexamine (Hexamethylenetetramine), $(CH_2)_6N_4$. M.W.=149·1.—A colourless, crystalline powder, having no odour. It sublimes at 263° C., with some decomposition, without melting. Solubility in water, 65; in alcohol, 8; the solutions are alkaline to litmus.

Determination.—Evaporate 0·5 gm. with 40 cc. of *N*/2 sulphuric acid on the water bath, treat the residue with water and continue the evaporation until the whole of the formaldehyde has been evolved. Dilute the residue with water and titrate the excess of sulphuric acid with *N*/2 sodium hydroxide solution to methyl red. 1 cc. *N*/2 NaOH ≡ 0·01752 gm. $(CH_2)_6N_4$.

Tests.—No residue should be obtained on ignition. The aqueous solution (5 per cent.) should not contain sulphates; neither should a coloration or precipitate be obtained on warming with Nessler's solution, showing the absence of ammonium salts and paraformaldehyde.

Homatropine Hydrobromide, $C_{16}H_{21}NO_3.HBr$. M.W.=356·1. (Homatropine, 77·3 per cent.).—White, odourless, crystalline powder. Soluble in water, 17·5 at 25° C.; less so in alcohol, 3·1 at 25° C.; slightly soluble in chloroform, 0·18 at 25° C. M.Pt. about 212° C., with partial decomposi-

tion. Homatropine itself melts at 98° to 100° C. Like atropine it gives a yellow to brick-red colour when warmed with 2 per cent. mercuric chloride in 60 per cent. alcohol. It does not yield a violet colour with Vitali's test (p. 131). Homatropine gives characteristic crystals with Wagner's reagent (see Appendix), or gold chloride.

Homatropine Hydrochloride. M.Pt. 217° to 219° C.—Its reactions are similar to homatropine hydrobromide.

Hydrastine, $C_{21}H_{21}O_6N$. M.W.=383·3.—Hydrastine is an alkaloid obtained from *Hydrastis canadensis*, and is a white, crystalline powder, insoluble in water. Soluble in alcohol, 0·8; in ether, 1·2; and in chloroform, 50. M.Pt. 132° C. A solution of hydrastine in dilute sulphuric acid develops an intense blue fluorescence on the addition of a few drops of potassium permanganate solution. Hydrastine gives no red colour with chlorine water (distinction from berberine).

Hydrastinine, $C_{11}H_{11}O_2N.H_2O$. M.W.=207·2.—This substance is an oxidation product of hydrastine. Forms white or yellowish crystals, insoluble in cold water, soluble in alcohol, ether, or chloroform. M.Pt. 116° to 117° C.

Hydrastinine Hydrochloride, $C_{11}H_{11}O_2N.HCl$. M.W.=225·6.—Pale yellow crystals, very soluble in water or alcohol, 33; only slightly soluble in ether or chloroform. M.Pt. about 210° C. The aqueous solution shows a blue fluorescence. A solution, when treated with Nessler's reagent, gives a precipitate which blackens instantly. (Morphine and apomorphine also give this.)

Hydrazine Sulphate, $NH_2.NH_2.H_2SO_4$. M.W.=130·1.—Forms glistening white plates, somewhat soluble in cold water, very soluble in hot water, insoluble in alcohol. M.Pt. 254° C. Practically no residue should remain after ignition.

Determination.—Dissolve 0·15 gm. in water, add 50 cc. of $N/10$ iodine solution and 1 gm. of sodium bicarbonate, and titrate the excess of iodine with $N/10$ thiosulphate solution. 1 cc. $N/10$ I ≡ 0·003253 gm. $N_2H_4.H_2SO_4$.

Hydrocyanic Acid, HCN. M.W.=27·0 (H, 3·74; CN, 96·26).—The acid is usually used as a 2 per cent. solution in water. An acid of this strength (S.G. 0·997) is official in the B.P.

Determination.—Dilute 5 cc. with 50 cc. of water, make alkaline with sodium hydroxide (5 cc. of a 5 per cent. solution), add a few drops of potassium iodide solution, and titrate with $N/10$ silver nitrate solution until the first appearance of a permanent precipitate. 1 cc. $N/10$ $AgNO_3$ ≡ 0·0054 gm. HCN. Common impurities are sulphates and chlorides. Non-volatile residue should not exceed 0·02 per cent.[1]

Hydroquinone, $C_6H_4\begin{cases}OH\ (1).\\ OH\ (4).\end{cases}$ M.W.=110·1.—Forms colourless crystals, without odour. Soluble in water, 6; easily soluble in alcohol or ether. M.Pt. 169° C. Ferric chloride added to the aqueous solution produces a blue coloration at first, and with excess of the reagent a crystalline precipitate of quinone or green crystals of quinhydrone. The aqueous solution should be free from sulphates and should not give a permanent violet coloration with ferric chloride, showing absence of phenol.

[1] For criticisms and alternative methods of determination, see *Y.B.P.*, 1920, 436; 1921, 391.

Hydroxylamine Hydrochloride, $NH_2.OH.HCl$. M.W.=69·5.—Clear, colourless crystals. Solubility in water, 60; in alcohol, 5.

Determination.—Treat 0·1 gm. with 10 cc. of a cold saturated solution of ferric ammonium sulphate and 20 cc. of dilute sulphuric acid (10 per cent.) for a few minutes; dilute with water and titrate the reduced iron with $N/10$ potassium permanganate. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·003475 gm. $NH_2.OH.HCl$.

Tests.—No residue should be left on ignition. Sulphates should be absent. A solution of 1 gm. in 20 cc. of alcohol should remain free from turbidity after adding a little platinum chloride solution and standing an hour (absence of ammonium salts).

Hyoscine Hydrobromide (*l*-Scopolamine hydrobromide), $C_{17}H_{21}NO_4.HBr.3H_2O$. M.W.=438·1. (Hyoscine, 69·2; water, 12·3.)—Forms colourless, transparent crystals. Hyoscine hydrobromide is *lævo*-rotatory, $[\alpha]_D$ about −25°. It loses about 12 per cent. of its weight at 100° C. Solubility in water, 66; in alcohol, 6; almost insoluble in chloroform.

Tests.—The alkaloid prepared by making alkaline with ammonia and extracting with chloroform melts at 56° to 57° C., gives the Vitali test (p. 131), and when dissolved in dilute hydrochloric acid gives a yellow precipitate with gold chloride, which has a characteristic crystalline form when examined microscopically. On recrystallising the aurichloride from water, the M.Pt. is 198° to 200° C. The microscopic form of the crystals formed with Wagner's reagent (see Appendix) may be also used as a method of identification.

Hyoscyamine Hydrobromide, $C_{17}H_{24}NO_3Br$. M.W.=370·1. (Hyoscyamine, 78·1.)—Gives white crystals, very soluble in water, less so in alcohol. M.Pt. 152° C. The free base melts at 108·5° C., gives Vitali's test (p. 131), and a crystalline aurichloride, M.Pt. 165° C. when pure; also a picrate, M.Pt. 161° to 164° C. $[\alpha]_D$ of hyoscyamine in alcoholic solution is about −20°. Hyoscyamine is very soluble in chloroform, but almost insoluble in petroleum ether, and only slightly soluble in ether.

Hyoscyamine Sulphate, $(C_{17}H_{23}NO_3)_2.H_2SO_4.2H_2O$. M.W.=712·5. (Hyoscyamine, 81·2; water, 5·0.)—A deliquescent, crystalline powder, very soluble in water, 200; soluble in alcohol, 22. M.Pt. 206° C. Its reactions are similar to those of the hydrobromide.

Iodoform, CHI_3. M.W.=393·8.—Small, lustrous crystals, having a yellow colour and a characteristic and persistent odour. M.Pt. 120° C. Solubility in water, 0·01; in alcohol, 2; in ether, 13.

Determination.—Heat 0·5 gm. with 50 cc. of $N/10$ silver nitrate solution in a flask for an hour under a reflux condenser, washing down any iodoform that collects in the condenser. Filter and titrate the unused silver nitrate with $N/10$ sodium chloride solution or $N/10$ ammonium thiocyanate solution. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·01312 gm. CHI_3.

Tests.—No residue should be left on ignition. The saturated aqueous solution should be colourless and not bitter to the taste, neutral to litmus and free from chlorides, iodides, and sulphates. It should dissolve to a clear solution in ten volumes of petroleum ether.

Isopropyl Alcohol, $(CH_3)_2CHOH$. M.W.=60·1.—A colourless liquid, miscible with water or ether, having no disagreeable odour either before or after evaporation. S.G. 0·790; B.Pt. 80·4° to 81·7° C. No pink colour should develop with decolorised fuchsine solution after standing for fifteen

minutes (absence of aldehydes). 5 cc. are mixed with 2 cc. of *N* sodium hydroxide and 5 drops of freshly prepared sodium nitroprusside solution. On making slightly acid with acetic acid no violet colour should form within one minute (absence of ketones).

Determination of Acetone.—10 cc. of the *iso*propyl alcohol are mixed with 10 cc. of *N*/2 solution of hydroxylamine hydrochloride in 80 per cent. alcohol and 8 cc. of *N*/2 alcoholic potassium hydroxide solution added, the mixture being allowed to stand in a stoppered bottle for two hours. It is then titrated first to phenolphthalein with *N*/2 potassium hydroxide solution and then to bromophenol blue with *N*/2 hydrochloric acid. A blank test is carried out at the same time, and the difference between the two titrations to bromophenol blue $\times 0{\cdot}029$ gives the weight of acetone in grams in the 10 cc. of *iso*propyl alcohol.[1]

Lactic Acid, $CH_3.CHOH.COOH$. M.W.=90·0.—A clear, colourless, syrupy liquid, having no odour. The B.P. acid is required to contain not less than 75 per cent. of lactic acid and not less than 10 per cent. of lactide, and to have S.G. 1·21. It is miscible in all proportions with water, alcohol, or ether; insoluble in benzene, chloroform, or carbon disulphide.

Determination.—Dilute 1 gm. with water, add 30 cc. of *N*/2 sodium hydroxide solution, warm gently for about ten minutes, and titrate back with *N*/2 hydrochloric acid to phenolphthalein. 1 cc. *N*/2 NaOH $\equiv$ 0·04503 gm. of $C_3H_6O_3$.

Tests.—On warming lactic acid with about three times its volume of dilute potassium permanganate solution the odour of acetaldehyde should be perceived. Sulphuretted hydrogen should cause no darkening when added to a 10 per cent. aqueous solution, neither should this solution give reactions for calcium, chloride, or sulphate. No turbidity should be produced on mixing lactic acid with ten times its volume of lime water, even on warming, showing the absence of oxalic, tartaric, and citric acids. On warming lactic acid with excess of zinc carbonate, drying at 100° C., extracting with alcohol, and evaporating the alcoholic extract to dryness, no sweet residue should be obtained, showing absence of glycerin. No darkening should be apparent on carefully pouring lactic acid over strong sulphuric acid in a test-tube, the temperature being kept low. On gradually adding lactic acid to twice its volume of ether no temporary or permanent turbidity should be produced, showing absence of sugars and other organic impurities. A 10 per cent. solution should not become turbid when mixed with a solution of copper sulphate (absence of sarcolactic acid), or with basic lead acetate solution (absence of malic acid, etc.).

Lactose (Milk Sugar), $C_{12}H_{22}O_{11}.H_2O$. M.W.=360·2. (Anhydrous lactose, 95·0; water, 5·0.)—A white powder, free from yellow colour or cheesy odour. The water of hydration is lost at 130° C., very slowly at 100° C. $[\alpha]_D = +52{\cdot}5°$ in a 10 per cent. solution. Solubility in water, 22; insoluble in alcohol, ether, or chloroform.

Determination.—Lactose may be determined by means of its optical rotation in the usual way, taking care to destroy bi-rotation, or by its reducing power, as given under Dextrose, using the table in Appendix.

Tests.—The mineral matter should not exceed 0·25 per cent. (B.P.), but the best samples show much less than this. Starch should be absent. 5 gm. dissolved in water should not require more than 1·5 cc. of *N*/10

[1] Simmons, *Perf. & Ess. Oil Rec.*, 1927, 168.

sodium hydroxide to phenolphthalein (limit of acidity, B.P.). Moisture is determined by drying at 100° C. for two hours and should not exceed 2 per cent., usually being much less than this. Nitrogen, determined by Kjeldahl's process, should be considerably less than 0·1 per cent.

Lævulose (Fructose; Fruit Sugar), $C_6H_{12}O_6$. M.W.=196·1.—Soluble in water; insoluble in alcohol or ether. M.Pt. of the anhydrous crystals, 95° C. Lævulose may be determined by the reduction method given under Dextrose (for Tables, see Appendix), or from the optical activity, $[\alpha]_D=-95°$. The optical rotation depends largely on the temperature, which fact distinguishes it from other sugars. It should be free from mineral matter, from barium, calcium, carbonate, chloride, and sulphate. Arsenic may be tested for as given under Glucose, p. 150.

Maltose (Malt Sugar), $C_{12}H_{22}O_{11}$. M.W.=342·2.—Maltose occurs as a white, amorphous powder, readily soluble in water or alcohol. The solution readily reduces Fehling's solution. $[\alpha]_D=+138°$ The characteristic appearance of the osazone distinguishes it from other sugars. On hydrolysis with acid, two molecules of dextrose are formed.

Menthol, $C_{10}H_{20}O$. M.W.=156·2.—Forms large, colourless crystals, having a characteristic odour. M.Pt. 42° to 43° C., B.P.; B.Pt. 212° C. Refractive index (45° C.)=1·450. The alcoholic solution is *lævo*-rotatory ($[\alpha]_D=-49·5°$ in 25 per cent. solution) and should be neutral to litmus. It is practically insoluble in water; solubility in alcohol (90 per cent.) about 600; soluble in ether, about 550; soluble also in chloroform, petroleum ether, or olive oil. It should be completely volatile on being heated on the water bath in an open dish (absence of paraffin, inorganic substances, etc.). It may be determined as given under Peppermint Oil (p. 319).

Synthetic Menthol occurs as colourless crystals, M.Pt. 28° to 30° C., or as a semi-liquid mass. It is usually optically inactive, but sometimes slightly *lævo*-rotatory.

Menthyl Valerate (Menthol Valerianate), $C_3H_7.COOC_{10}H_{19}$. M.W.= 226·2.—Menthyl valerate, also known as *Validol*, as used in medicine, contains a proportion of free menthol. It is a not unpleasant smelling, colourless liquid, with the following characteristics: S.G. 0·904 to 0·910; refractive index at 20° C., about 1·45. Free valeric acid should be absent, but if present may be determined by titration in alcoholic solution to thymol blue. 1 cc. $N/10$ KOH ≡ 0·0102 gm. $C_5H_{10}O_2$. Menthyl valerate is saponifiable with difficulty, and for its determination by this method 2·5 gm. should be boiled with 25 cc. of N alcoholic potash for six hours. 1 cc. $N/2$ KOH ≡ 0·01131 gm. $C_3H_7COOC_{10}H_{19}$. Not less than 70 per cent. should be present. Total menthol may be determined by acetylation (see p. 309).

Methanol (Methyl Alcohol), CH_3OH. M.W.=32·0.—A colourless, mobile liquid, having a pleasant, spirituous odour. B.Pt. 66° C.; S.G. 0·796. Miscible in all proportions with water, alcohol, ether, chloroform, fixed or essential oils.

Determination.—It may be determined when in aqueous solution by the S.G.;[1] when mixed with impurities by conversion into methyl iodide,[2] and when in the presence of ethyl alcohol by the method of Thorpe and Holmes.[3] Methanol may be detected and determined when present in

[1] *J. Soc. Chem. Ind.*, 1910, **29**, 173.
[2] *Ber.*, 1874, **7**, 1492.
[3] *J. Chem. Soc.*, 1904, **85**, 1.

ethyl alcohol by oxidation to formaldehyde and the use of Schiff's reagent, as suggested by Simmonds [1] (see also p. 146).

Tests.—Methanol should volatilise completely on the water bath, evolve no foreign odour at any stage of the evaporation, and leave no residue. It should be neutral to litmus, and should mix with water to form a perfectly clear solution. 5 cc. diluted with water and treated with sodium hydroxide and iodine should not develop any iodoform (absence of ethyl alcohol and acetone). If present, acetone may be determined by the method of Auld.[2] Methanol should remain colourless on shaking with an equal volume of 30 per cent. sodium hydroxide solution. The gradual addition to 5 cc. of methyl alcohol of an equal volume of strong sulphuric acid, keeping the liquid cool, should only result in the production of the faintest yellow coloration.

Methyl Salicylate, $C_6H_4.OH.COOCH_3$. M.W.=152·1.—A colourless liquid, having a characteristic odour. S.G. 1·185 to 1·192 (B.P.). B.Pt. 219° to 221° C. (B.P.). Slightly soluble in water; easily soluble in alcohol, ether, chloroform, glacial acetic acid, or carbon disulphide.

Determination.—Methyl salicylate may be determined by saponification (see p. 145). 1 cc. $N/2$ KOH ≡ 0·07605 gm. $C_6H_4OH.COOCH_3$. The B.P. requires that it shall contain not less than 98 per cent. of pure methyl salicylate.

Tests.—Salicylic acid should be separated in the usual manner and tested for its purity. No portion should boil much below 220° C. (absence of alcohol, chloroform, etc.). 1 cc. should be dissolved by 5 cc. of potassium hydroxide solution (10 per cent.) to a perfectly clear solution.

Methyl Sulphonal (*Trional*), $C_8H_{18}S_2O_4$. M.W.=424·2.—Forms white, shining crystals, slightly soluble in water, 0·31, more soluble in alcohol, 9. No odour should be noticed on boiling with water, and 100 cc. of a cold, saturated, aqueous solution should not immediately decolorise one drop of a 0·1 per cent. solution of potassium permanganate. M.Pt. 76° C. No appreciable ash.

Methylene Blue, $C_{16}H_{18}N_3SCl.3H_2O$. M.W.=373·8.—Methylene blue is a dark blue powder. Solubility in water, 2; less soluble in alcohol.

Determination.—Where necessary it may be determined by means of titanous chloride,[3] or by the method of Atack.[4] Not more than 1 per cent. of mineral matter should be present. 0·5 gm. on gentle ignition, the residue being boiled with 10 cc. of hydrochloric acid and filtered and made alkaline with ammonia, should show no turbidity on the addition of sodium sulphide solution, showing absence of zinc.

Arsenic.—Fuse 0·2 gm. with 0·5 gm. each of potassium nitrate and sodium carbonate, dissolve the residue in 15 cc. of dilute sulphuric acid, evaporate until fumes are evolved, add 50 cc. of warm water, 10 cc. of stannated hydrochloric acid, and proceed as usual. It may be determined directly by the electrolytic method.

Morphine, $C_{17}H_{19}NO_3.H_2O$. M.W.=303·2. (Anhydrous morphine, 94·1, water, 5·9).—Forms white, needle-shaped crystals. It loses its water of crystallisation slowly at 100° C., and when anhydrous melts at about

[1] *Analyst*, 1912, **37**, 18; *cf.* Jones, *ibid.*, 1915, **40**, 218.
[2] *J. Soc. Chem. Ind.*, 1906, **25**, 100.
[3] Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis.*
[4] *J. Soc. Dyers & Col.*, 1913, **29**, 9.

247° C. with decomposition. Solubility in water, 0·028; in ethyl alcohol, 0·39; in methyl alcohol, 6·7; in ether, 0·013; in chloroform, 0·05; in amyl alcohol, 0·88; in petroleum ether, 0·085; insoluble in benzene; soluble in benzyl alcohol, 21·8. Morphine is a phenol and dissolves in strong alkalis, but is only slightly soluble in ammonia, the solubility depending on the concentration of hydroxyl ions present.

Tests.—Morphine gives an orange-red colour with nitric acid. With ferric chloride in neutral solution a greenish-blue colour is observed. A solution of morphine added to a dilute solution of potassium ferricyanide containing a trace of ferric chloride gives a deep blue colour. Froehde's reagent (see Appendix) produces a deep purple colour, which is also formed if morphine is treated with sulphuric acid containing 1 drop of solution of formaldehyde per cc. Morphine gives very characteristic crystals with Marme's reagent (see Appendix) in dilute solutions. Owing to its slight solubility morphine can only be removed with difficulty from slightly alkaline solutions by means of immiscible solvents; from strongly alkaline solutions or from acid solution it is not extracted at all. Hot amyl alcohol is the best solvent, slight excess of ammonia being added after the amyl alcohol and the whole immediately shaken. Morphine may be titrated by dissolving in excess of standard acid, and titrating back with alkali, using methyl red to an orange colour. 1 cc. $N/10$ acid ≡ 0·0285 gm. morphine.

Morphine Acetate, $C_{17}H_{19}NO_3.C_2H_4O_2.3H_2O$. M.W.=399·2. (Anhydrous morphine, 71·4; water, 13·5.)—A white, crystalline, or amorphous powder, usually having an odour of acetic acid. Morphine acetate loses acetic acid on keeping, and becomes less soluble in water. When freshly prepared, or if containing an excess of acetic acid, it is very soluble in water (about 40). In any case 2 gm. with 5 cc. of warm water should give a slightly turbid solution, which becomes clear on the addition of 2 drops of 33 per cent. acetic acid (B.P.).

Determination.—1 gm. dissolved in 25 cc. of morphinated water yields, on bringing the pH value to 9 by the addition of ammonia (so that thymol blue just gives a blue colour), a white precipitate which, after standing overnight, washing with a little morphinated water, and drying first at 55° to 60° C., and finally at 115° C. until constant in weight, shows 70·5 to 72 per cent. of anhydrous morphine.

Tests.—As under Morphine.

Morphine Hydrochloride, $C_{17}H_{19}NO_3.HCl.3H_2O$. M.W.=375·7. (Anhydrous morphine, 75·7; water, 14·4.)—A white, microcrystalline powder. Solubility in water, 5; in alcohol, 2. Moisture content about 14 per cent.

Determination.—1 gm. treated as "Morphine Acetate" shows 75 to 76 per cent. morphine (B.P.). The morphine obtained by this method should yield not more than a trace of soluble matter to benzene, and show the reactions given under Morphine.

Morphine Sulphate, $(C_{17}H_{19}NO_3)_2.H_2SO_4.5H_2O$. M.W.=758·5. (Anhydrous morphine, 75·2; water, 11·9.)—Forms white, feathery crystals or cubical masses, soluble in water, 4·2, less soluble in alcohol, 0·14. The percentage of morphine, determined as under Morphine Acetate, is about 75 per cent. The morphine obtained should respond to the tests for purity given under Morphine.

Morphine Tartrate, $(C_{17}H_{19}NO_3)_2.C_4H_6O_6.3H_2O$. M.W.=774·4. (An-

hydrous morphine, 73·6; water, 7·0.)—Gives minute, acicular crystals, efflorescent at 20° C. Soluble in water, 10; slightly soluble in alcohol, 0·17. Morphine is determined as under Morphine Acetate, and should amount to 73 to 74·5 per cent. (B.P.). The morphine obtained should respond to the tests for purity given under Morphine.

Naphthalene, $C_{10}H_8$. M.W.=128·1.—M.Pt. 80° C.; B.Pt. 218° C.; S.G. 1·152. It should be completely volatile on ignition. Insoluble in water; soluble in alcohol, 5·3; readily soluble in ether, benzene, or toluene.

Tests.—Heating with sulphuric acid should only result in a faint rose colour. It should remain colourless for at least half an hour when exposed on a watch-glass to the fumes of conc. (not fuming) nitric acid under a bell jar. It should be free from phenols, which may be tested for by boiling with dilute sodium hydroxide solution, cooling, filtering, and adding to the filtrate hydrochloric acid and bromine water; in the presence of phenols the bromine compounds will be precipitated. It may be determined if necessary by sublimation,[1] or by the insoluble compound formed with picric acid.[2]

Narcotine, $C_{22}H_{23}NO_7$. M.W.=413·2.—Forms colourless prisms or long needles. Insoluble in water; somewhat soluble in alcohol and ether; soluble in benzene and chloroform. M.Pt. 176° C.

Tests.—Sulphuric acid dissolves narcotine with the formation of a pale yellow solution which gradually turns red. Narcotine is a very weak base, and the salts are very unstable. It occurs in opium in considerable proportion, and may be determined by the method of Rakshit.[3]

Nicotine, $C_{10}H_{14}N_2$. M.W.=162·1.—A hygroscopic, colourless, or yellowish-brown liquid, with the unpleasant odour of stale burnt tobacco. B.Pt. 240° to 242° C. Refractive index (15° C.) 1·530. Very soluble in water, alcohol, or ether.

Determination.—Nicotine may be titrated with $N/2$ HCl to methyl red. 1 cc. $N/2$ HCl $\equiv$ 0·08105 gm. $C_{10}H_{14}N_2$.

Tests.—Adulteration of commercial nicotine with pyridine is a possibility. It may be detected by the refractive index, combined with the boiling-point observation and titration.[4] Nicotine forms characteristic crystals with gold chloride in very high dilution; even a 1:15,000 solution gives a small number of crystals.

Nitrobenzene, $C_6H_5NO_2$. M.W.=123·1.—M.Pt. 3° C.; B.Pt. 207° C.; S.G. 1·209. Insoluble in water; miscible in all proportions with alcohol, ether, and benzene.

Tests.—In the examination of commercial samples the S.G. and the B.Pt. are usually determined. The former should not be less than 1·20, whilst at least 95 per cent. should distil between 204° and 208° C. Concentrated sulphuric acid should have practically no action.

Nitroglycerin, $C_3H_5(NO_3)_3$. M.W.=227·1.—A liquid, colourless when pure, though frequently yellowish. Solidifies at 8° C. Very slightly soluble in water, but easily soluble in alcohol, ether, or chloroform. It is official in the B.P. as *Liq. Trinitrini* (see p. 254), a 1 per cent. solution in alcohol. It is highly explosive.

[1] White and Hall, *Gas Lighting*, 1904, **88**, 262, 326.
[2] Küster, *Ber.*, 1894, **27**, 1101.
[3] *Analyst*, 1921, **46**, 481.
[4] P. J. Fryer and C. H. Fryer, *Analyst*, 1919, **44**, 363.

Determination.—Add 0·2 cc. of 7·5 *N* NaOH to 5 cc. of *Liq. Trinitrini* in a corked test-tube. After one-half to two hours pour into the cup of a nitrometer filled with saturated brine, rinse the tube with small amounts of alcohol, and add 5 cc. of 10 per cent. potassium iodide solution, and then 5 cc. of 3*N* sulphuric acid. Shake till evolution of gas ceases, measure the gas, and correct to N.T.P. The number of cc. at N.T.P.×0·1062= w/v $C_3H_5(NO_3)_3$.

Novarsenobenzene (*Neosalvarsan, Neokharsivan, Novarsenobillon,* Neoarsphenamine), $NH_2(OH)C_6H_3.As.As.C_6H_3(OH)NH.(CH_2O)SO.Na$. M.W.= 466·1.—A yellow to orange-yellow, dry powder. 0·6 gm. should dissolve rapidly and completely in 1 cc. of water, forming a yellow coloured, clear solution, mobile, non-gelatinous, and free from suspended particles. The 5 per cent. solution is neutral to litmus paper.

Arsenic.—When determined as under Arsenobenzene (p. 129), the arsenic should not be less than 18 per cent., and not more than 21 per cent.

Nucleic Acid.—The preparation known in pharmacy as nucleic acid (sometimes erroneously termed nuclein) is prepared from yeast, and consists of true nucleic acid with protein products and some carbohydrate. It is a light, yellowish-brown powder, slightly soluble in water, and completely soluble in alkalis. The acid is precipitated from this solution on the addition of hydrochloric acid, and redissolves in a large excess of conc. hydrochloric acid.

Biuret Test.—A solution in potassium hydroxide gives on the addition of 1 or 2 drops of dilute copper sulphate solution a greenish-blue colour with at the most a tinge of purple.

Inorganic Phosphate.—If dissolved in a large excess of sodium acetate, the addition of a few drops of acetic acid, followed by a little uranium acetate, gives a flocculent precipitate, which dissolves on boiling.

Nitrogen is determined on 0·5 gm. by Kjeldahl's method. Not less than 15 per cent. should be present.

Phosphorus.—1 gm. is fused with fusion mixture, dissolved in water, and acidified with nitric acid. The phosphate is then determined in the usual way. Not less than 9 per cent. should be present.[1]

Oleic Acid, $C_{17}H_{33}.COOH$. M.W.=282·4.—A yellow, oily liquid, odourless, or with a faintly rancid odour. S.G. 0·898; solidifying-point, 4° C.; M.Pt. 6·5° C. Refractive index (25° C.), 1·460. The B.P. requires S.G. 0·890 to 0·910, and solidifying-point below 9° C. Insoluble in water, miscible in all proportions with alcohol, ether, chloroform, or fixed oils. The alcoholic solution should be perfectly clear and bright. No residue should be obtained on ignition.

Determination.—Titrate 5 gm. in alcoholic solution with *N*/2 sodium hydroxide to thymol blue or phenolphthalein. 1 cc. *N*/2 NaOH ≡ 0·1411 gm. $C_{17}H_{33}COOH$. The acidity so determined is not necessarily oleic acid; a result of more than 100 per cent. will point to the presence of lower fatty acids, and *vice versa.*

Oxalic Acid, $(COOH)_2.2H_2O$. M.W.=126·1.—Forms colourless crystals which melt in their water of crystallisation at 98° C., gradually becoming anhydrous at that temperature. Solubility in water, 8·5; in alcohol, 26; slightly soluble in ether, chloroform, etc.

Determination.—Titrate 0·18 gm. with *N*/10 sodium hydroxide to phenol

[1] *Cf.* Chapman, *Analyst,* 1918, 43, 259.

red (1 cc. $N/10$ NaOH $\equiv$ 0·006305 gm. $C_2H_2O_4.2H_2O$), or titrate the same weight, after acidifying with sulphuric acid, with $N/10$ potassium permanganate at a temperature of about 50° C. 1 cc. $N/10$ $KMnO_4 \equiv$ 0·006305 gm. $C_2H_2O_4.2H_2O$.

Tests.—No residue should be obtained on ignition. It should be free from heavy metals, ammonia, chloride, and sulphate. The aqueous solution should be perfectly clear and bright, and without sediment.

Paraffin, Liquid (*Paraffinum liquidum*, B.P.).—A mixture of liquid hydrocarbons. It is a transparent, colourless, non-fluorescent, odourless, tasteless liquid. S.G. 0·860 to 0·890 (B.P.). These limits are too wide, and the S.G. of a good medicinal paraffin should not be below 0·880.

Viscosity.—50 cc. at 100° F. should flow through a Redwood viscometer (see p. 284) in not less than 200 sec. Many of the higher class paraffins require up to 300 sec.

Tests.—When 3 cc. are heated with an equal volume of sulphuric acid in a tube immersed in boiling water for ten minutes with frequent shaking, the acid layer is coloured not darker than pale brown (B.P.).

Sulphur Compounds.—A mixture of 4 cc. of paraffin with 2 cc. of absolute alcohol and 2 drops of a clear, saturated solution of lead oxide in a solution of sodium hydroxide remains colourless when kept at 70° C. for ten minutes (B.P.). Liquid paraffin should remain bright at 0° C. 10 cc. of neutral 90 per cent. alcohol boiled with 5 cc. of liquid paraffin should not become acid to methyl red.

Paraffin, Soft (*Paraffinum molle*, B.P., Petroleum Jelly).—A mixture of semi-solid hydrocarbons. It is translucent, soft, unctuous, and uniform. The "white" variety is almost white, and certainly not deeper than very pale yellow. No odour should be observed when a little is rubbed on the skin. The yellow variety is not usually free from odour when tested in this way, but the odour should not be unpleasant even on heating to 80° C. M.Pt. 42° to 46° C. The M.Pt. is very indefinite, and may be best determined by melting about 10 gm. in a test-tube, stirring with a thermometer, and noting the range over which solidification occurs.

Tests.—When 5 gm. are boiled with 10 cc. of neutral 90 per cent. alcohol the alcohol should not be acid to methyl red. When 10 gm. are boiled with 20 cc. of sodium hydroxide solution for ten minutes and allowed to separate, the aqueous layer yields no precipitate or oily matter when acidified with dilute sulphuric acid. The ash should be inappreciable.

Paraffin Wax (*Paraffinum durum*, B.P., Hard Paraffin).—A mixture of solid hydrocarbons. Colourless, translucent masses, slightly greasy to the touch. Odourless when freshly broken. M.Pt. 50° to 60° C. (B.P.). If 5 gm. of melted paraffin are shaken with 5 cc. of neutral 90 per cent. alcohol, the latter does not become acid to methyl red. Ash inappreciable.

Paraformaldehyde (*Trioxymethylene*), $C_3H_6O_3$. M.W.=90·0.—A white, amorphous powder, insoluble in water. It is dissolved and decomposed by boiling water with the production of formaldehyde. On heating it is decomposed to formaldehyde. For the determination of paraformaldehyde in tablets see p. 149.

Paraldehyde, $C_6H_{12}O_3$. M.W. = 132·1.—A polymerised product of acetaldehyde. Colourless liquid of ethereal odour. S.G. 0·998 to 1·000 (B.P.). M.Pt. not less than 10° C. B.Pt.—not more than 5 per cent. distils below 123° C., the greater part distilling between 123° and 125° C.

Solubility in water, 11; miscible in all proportions with alcohol or ether. 1 cc. dissolved in 10 cc. of water is not acid to methyl red. Should be tested for chloride and sulphate. If 5 cc. are shaken with 5 cc. of 20 per cent. sodium hydroxide solution, and allowed to separate, the aqueous layer does not become more than faintly yellow in one hour (test for acetaldehyde).

Determination of Acetaldehyde.[1]—Mix 10 cc. of $N/10$ mercuric chloride solution, 2 gm. of potassium iodide, 20 gm. of 15 per cent. sodium hydroxide solution, 50 gm. of water, and 5 cc. of paraldehyde, and shake occasionally during fifteen minutes, then dilute to 100 cc., and filter. Treat 50 cc. of the filtrate with 0·5 gm. of powdered gum arabic, 5 cc. of sodium hydroxide solution, and 3 cc. of formaldehyde; after fifteen minutes acidify the mixture with 15 cc. of dilute acetic acid, cool, dissolve the reduced mercury by the addition of 10 cc. of $N/10$ iodine solution, and titrate the excess of iodine with $N/10$ thiosulphate solution. The number of cc. of iodine solution used by the mercury is multiplied by 2, and subtracted from the number of cc. iodine solution equivalent to 10 cc. of the mercuric chloride solution. 1 cc. $N/10$ iodine $\equiv$ 0·0022 gm. acetaldehyde.

Pelletierine, $C_8H_{15}NO$. M.W.=141·1.—A liquid alkaloid obtained from the root bark of *Punica granatum* (pomegranate). A colourless, oily liquid with a wine-like odour. It becomes brown in the air. B.Pt. 195° C. with decomposition. Soluble in water, 4·3, and in all proportions in alcohol, ether, or chloroform.

Pelletierine Tannate.—A light yellow, amorphous powder, slightly soluble in water, more soluble in alcohol. At 150° C. pelletierine tannate turns brown, and softens at 165° C. At higher temperatures it decomposes without melting. The solution gives the usual tests for tannic acid (*q.v.*). The ash should be inappreciable.

Petroleum Spirit (Petroleum Ether).—A colourless, mobile, volatile, and highly inflammable liquid, consisting of a mixture of the lower members of the series of paraffin hydrocarbons; it is one of the first liquid fractions obtained in the distillation of American Petroleum. B.Pt. 40° to 70° C.; S.G. about 0·665. The B.P. requires B.Pt. 50° to 60° C., and S.G. 0·670 to 0·770.

Tests.—Various qualities are sold according to their boiling-points. 10 cc. shaken with an equal quantity of water should not impart an acid reaction to the latter. No residue should be obtained on evaporation to dryness, and no permanent oily stain should be obtained on allowing one drop to fall on a piece of clean white paper.

Phenacetin, $C_6H_4\left\langle\begin{matrix}OC_2H_5\,(1)\\NH\,.\,COCH_3\,(4).\end{matrix}\right.$ M.W.=179·1.—Forms small, colourless, glistening crystals, without odour or taste. M.Pt. 135° C. Solubility in water, 0·07, more soluble in hot water; in alcohol, 6·5; soluble in ether.

Tests.—No residue should be obtained on ignition. No colour should be produced on dissolving phenacetin in strong sulphuric acid. A cold, saturated, aqueous solution should not become turbid on the addition of bromine water (absence of phenol and acetanilide). About 0·5 gm. dissolved in 2 cc. of alcohol should not acquire a rose-red tint on adding several cc. of $N/1000$ solution of iodine (absence of *para*phenetidine). A method for

[1] Stuve, *Apoth. Zeit.*, 1920, **35**, 145.

the determination of phenacetin has been suggested by Turner and Vanderkleed.[1]

Phenazone (*Antipyrine*), $C_{11}H_{12}N_2O$. M.W.=188·1.—Forms colourless, odourless, crystalline plates. M.Pt. 112° C. The B.P. gives 111° to 113° C. Solubility in water, 80; in alcohol, 93; in ether, 3·5; in chloroform, 75. Phenazone may be determined by means of its insoluble iodine compound, either volumetrically or gravimetrically.[2] The aqueous solution should be clear and bright, neutral to litmus, and not affected by hydrogen sulphide. Ferric chloride solution gives a red colour. No residue should be obtained on ignition. A small quantity warmed with a little sodium hydroxide solution and a few drops of chloroform should not develop the odour of phenyl *iso*nitrile (absence of acetanilide). The aqueous solution should not be affected by a solution of silver nitrate.

Phenazone Salicylate (*Salipyrin*), $C_{18}H_{18}N_2O_4$. M.W.=326·2.—A white, crystalline, odourless powder. M.Pt. 92° C. Solubility in water, 0·4; more soluble in boiling water, 4; in alcohol, 25. Very soluble in ether or chloroform. Ash, nil.

Tests.—A saturated aqueous solution gives a green colour with a few drops of fuming nitric acid. Ferric chloride gives a violet colour.

Determination of Phenazone.—Dissolve 1 gm. in 40 cc. of hot water, add 10 cc. of *N* NaOH solution, and shake out the phenazone with four quantities each of 15 cc. of chloroform. Evaporate off the chloroform, and weigh the residue. Theoretical content, 57·7 per cent.

The salicylic acid may be determined in the aqueous liquid as under Sodium Salicylate. Theory, 42·3 per cent.

Phenol (Carbolic Acid), C_6H_5OH. M.W.=94·0.—Forms colourless, somewhat deliquescent crystals, which have a tendency to become pink on exposure to light. M.Pt. 42° C. when pure. (The B.P. gives 39° to 40° C.) B.Pt. not higher than 183° C. S.G. at the M.Pt. 1·060 to 1·066. When evaporated on the water bath, not more than 0·1 per cent. of residue should remain. Solubility in water, 8; very soluble in alcohol, glycerin, ether, or chloroform. At 15·5° C. 10 parts of phenol are liquefied by the addition of one part of water and completely dissolve 3 to 4 parts of water.

Determination.—Into a 500 cc. stoppered bottle place 60 cc. of water, 5 cc. of hydrochloric acid, and 0·1 gm. of phenol dissolved in 10 cc. of water. Run in quickly from a burette sufficient *N*/10 bromide-bromate solution (see Appendix) to make the solution yellow, and then add 10 per cent. more. Shake continuously for one minute. Add 5 cc. of 10 per cent. potassium iodide solution, and titrate the liberated iodine with *N*/10 thiosulphate solution. Carry out a blank titration on the same volume of bromide-bromate solution. 1 cc. *N*/10 bromide-bromate ≡ 0·001568 gm. phenol. 10 cc. of phenol and 1 cc. of water form a clear liquid with 10 cc. of glycerin, not rendered turbid by adding 30 cc. of water (absence of cresol). An aqueous solution should not be acid to methyl red.

Acidum Carbolicum Liquefactum (Liquefied Phenol, B.P.) is phenol liquefied by the addition of 15 gm. of water to 100 gm. of phenol. It should form a clear solution on the addition of 12 to 20 per cent. of water by weight at 15·5° C. S.G. 1·067 to 1·069; B.Pt. not above 183° C.

[1] Abs., *J. Soc. Chem. Ind.*, 1907, **26**, 486; *Y.B.P.*, 1907, 4.

[2] Kipperberger, *J. Soc. Chem. Ind.*, 1896, **15**, 266, and Astne, *ibid.*, 1912, **31**, 898; *Y.B.P.*, 1913, 350.

Phenolphthalein (Dihydroxydiphenylphthalide), $C_{20}H_{14}O_4$. M.W.=318·1. —A white or yellowish white powder, practically insoluble in water, but soluble in alcohol, 7·5, giving a colourless, clear solution. M.Pt. 250° to 253° C. (B.P.); not below 253° C. (U.S.P.). Ash, nil. 0·5 gm. should dissolve completely in 4 cc. of 20 per cent. sodium hydroxide solution and 50 cc. of water. If 0·5 cc. of a 1 per cent. solution in 60 per cent. alcohol is added to 250 cc. of boiled and cooled distilled water, not more than 0·1 cc. of $N/10$ sodium hydroxide solution should be required to produce a pink colour.

Phenyl Ethyl Barbituric Acid [*Luminal*; Phenobarbital (U.S.P.)], $(C_6H_5)(C_2H_5)C.(NHCO)_2.CO$. M.W.=232·2.—White, odourless crystals. Slightly soluble in water, 0·1; soluble in chloroform, 40; in ether, 13; and in alcohol, 8. M.Pt. 173° to 175° C. Ash, negligible. 0·2 gm. dissolved in 2 cc. of cold sulphuric acid should not give more than a faintly yellow solution. 2 gm. boiled with 10 cc. of alcohol for three minutes under a reflux condenser should be completely soluble (absence of phenyl barbituric acid).

Determination.—See Barbitone, p. 131.

Phenylhydrazine, $C_6H_5NH.NH_2$. M.W.=108·1.—A colourless, crystalline mass, melting at 23° C. to a slightly yellow oil becoming red or brown on exposure to air. B.Pt., with slight decomposition, 241° to 242° C. Slightly soluble in water, readily soluble in alcohol or ether. 2 gm. dissolve in 20 cc. of 5 per cent. acetic acid to a clear solution.

The *Hydrochloride* $(C_6H_9N_2Cl$. M.W.=144·5) is found as lustrous plates usually of a pinkish tinge, easily soluble in water or alcohol.

Tests.—Phenylhydrazine salts reduce silver, mercury, gold, and platinum salts in the cold, and also Fehling's solution. With aldehydes and ketones in the presence of sodium acetate, oily or crystalline compounds are produced, those of the sugars in particular have characteristic crystalline forms, which may be used as a means of identification. Phenylhydrazine may be determined by Causse's method.[1]

Physostigmine (*Eserine*), $C_{15}H_{21}N_3O_2$. M.W.=275·2.—An alkaloid of calabar bean. It is used in the form of the *salicylate* $(C_{15}H_{21}N_3O_2.C_7H_6O_3$. M.W.=413·2) and as the *sulphate* $[(C_{15}H_{21}N_3O_2)_2.H_2SO_4$. M.W.=648·5]. Physostigmine salts dissolve in nitric acid forming a yellow solution, which on warming becomes red, and on evaporation to dryness leaves a green residue. When evaporated to dryness with ammonia, a bluish residue remains, which on dissolving in alcohol and acidifying with dilute acetic acid gives a red fluorescent solution. Potassium hydroxide gives a deep pink colour with physostigmine salts. The salicylate is slightly soluble in water, 0·75, more soluble in alcohol, 8. The sulphate is a yellowish-white, deliquescent powder, and is very soluble in water or alcohol.

Picric Acid (Trinitrophenol), $C_6H_2OH(NO_3)_3$. M.W.=229·0.—A bright yellow, crystalline powder. Soluble in water, 1·1; in alcohol, 10; in ether, 15. M.Pt. 122·5° C. It may be determined by titrating 2 gm. with $N/2$ sodium hydroxide solution to methyl red. 1 cc. $N/2$ NaOH ≡ 0·1145 gm. picric acid. Sulphates should be inappreciable. No appreciable ash should remain on ignition. The ignition is carried out by adding the substance, a little at a time, to a heated crucible fixed in an inclined position. Under certain circumstances the acid is highly explosive.

Picrotoxin, $C_{30}H_{34}O_{13}$. M.W.=602·3.—A neutral principle from *Cocculus*

[1] *Compt. rend.*, 1898, **125**, 712.

Indicus. Picrotoxin is an odourless, poisonous, white, crystalline powder, slightly soluble in water, 0·3; more soluble in boiling water, 3; in cold alcohol, 7·5; in boiling alcohol, 33; and in ether and chloroform. It is also readily dissolved by potassium hydroxide solution. M.Pt. when pure, 199° to 200° C., but often somewhat below this.

Pilocarpine, $C_{11}H_{16}O_2N_2$. M.W.=208·2.—This is the chief alkaloid of Jaborandi leaves. It is a colourless, syrupy liquid, and is chiefly used in the form of its salts. $[\alpha]_D = -100{\cdot}5°$ in chloroform. Pilocarpine is readily soluble in water, alcohol, or chloroform, but almost insoluble in ether or petroleum ether. Pilocarpine is readily changed to *iso*pilocarpine by heat or by alkalis. *Iso*pilocarpine occurs in varying quantity in the commercial alkaloid and its salts.

Tests.—On dissolving 0·01 to 0·02 gm. of pilocarpine or its salts in 2 cc. of water, adding 2 cc. of hydrogen peroxide solution, and covering the mixture with a little benzene, the addition of 3 or 4 drops of *N*/10 solution of potassium dichromate causes the production, on shaking, of a violet colour in the benzene layer, while the aqueous layer remains yellow. Pilocarpine picrate melts at 147° C. The platinichloride and aurichloride form crystalline precipitates.

Pilocarpine Hydrochloride, $C_{11}H_{16}N_2O_2.HCl$. M.W.=244·6.—Forms colourless, translucent, hygroscopic crystals. Very soluble in water, 330; in alcohol, 4·3 at 25° C.; slightly soluble in chloroform, 0·18 at 25° C. M.Pt. (when dried at 100° C.) 195° to 198° C. See also Pilocarpine.

Pilocarpine Nitrate, $C_{11}H_{16}O_2N_2.HNO_3$. M.W.=271·2.—White crystals or a microcrystalline powder. Soluble in water, 25 at 25° C.; in alcohol, 1·66 at 25° C. M.Pt., when pure, 177° to 178° C. The B.P. gives about 176° C., and the U.S.P. 170° to 173° C. The M.Pt. is lowered by the presence of *iso*pilocarpine. See also Pilocarpine.

Piperazine, $C_4H_{10}N_2$. M.W.=86·1.—Forms colourless crystals, readily soluble in water, giving a strongly alkaline solution. M.Pt. (anhydrous) 104° to 107° C.; but the compound often occurs as the hexahydrate (M.Pt. 44° C.).

Tests.—On the addition of a saturated solution of picric acid the picrate is precipitated as pale yellow needles of characteristic microscopic appearance. Potassium bismuth iodide gives a yellow precipitate, amorphous at first, but changing to golden yellow scales.

Pyrogallol, $C_6H_3(OH)_3$. M.W.=126·1.—A very light, white, crystalline powder. Solubility in water, 59; in alcohol, 100 at 25° C.; and in ether, 91 at 25° C. M.Pt. 131° C. On making the solution alkaline it absorbs oxygen from the air and becomes dark brown. The ash should be negligible. For the colorimetric determination of pyrogallol, see Mitchell.[1]

Quinidine Sulphate, $(C_{20}H_{24}N_2O_2)_2.H_2SO_4.2H_2O$. M.W.=782·7 (Quinidine, 82·9; water, 4·6).—White, silky needles, or long, hard prisms. Slightly soluble in water, 1·0; in alcohol, 7; in chloroform, 5. The solution in water acidified with sulphuric acid shows a blue fluorescence. M.Pt. 206° C.

Tests.—Not more than 5 per cent. in weight should be lost at 120° C. The *p*H value of a saturated aqueous solution should be between 5 and 6.

Determination of Other Alkaloids.—Dissolve 0·5 gm. in 10 cc. of water at

[1] *Analyst,* 1923, **48**, 2.

60° C., add 0·5 gm. of potassium iodide (free from alkaline reaction), allow to stand for thirty minutes with frequent shaking, and filter. 1 or 2 drops of ammonia solution should cause not more than a slight turbidity in the filtrate. If a decided precipitate forms, shake with chloroform, evaporate the solvent, dry the residue at 110° C., and weigh. The precipitated hydriodide should be sandy, not resinous. Commercial quinidine sulphate always contains a large amount of hydroquinidine sulphate, but this has a similar physiological activity.

Quinine, $C_{20}H_{24}O_2N_2.3H_2O$. M.W.=378·3. (Anhydrous quinine, 85·7; water, 14·3.)—Quinine is a white, soft, flaky powder. It loses two molecules of water at 100° C. and becomes anhydrous at 125° C. It should not lose more than 14·3 per cent. of its weight at 125° C. Solutions of quinine in sulphuric, acetic, or tartaric acids show a strong blue fluorescence which persists even at very high dilutions. Quinidine and hydroquinine also give a blue fluorescence, but cinchonine, cinchonidine, and cupreine do not. The presence of hydrochloric acid destroys the fluorescence. Solubility in water, 0·057; in alcohol, 100; in ether, 22; in chloroform, 52. Hydrated quinine melts at 57° C., but when anhydrous the M.Pt. is 172° C.

Thalleioquin Test.—This is the chief of the colour tests for quinine. Unless carefully carried out it is uncertain in its indications. A good method is to take 10 cc. of the quinine solution and add 0·5 cc. of saturated bromine water. Shake and then add 1 drop of strong ammonia solution, or sufficient to render the liquid distinctly alkaline. In the more concentrated solutions a green precipitate is thrown down, but usually a deep green colour is formed. La Wall [1] has stated that if the test is carried out according to the following method it is possible to detect 1 : 200,000 of quinine: 100 cc. of a solution to be tested, at a dilution of 1 : 100,000 or less, are poured into a Nessler tube; 5 to 10 drops of a reagent prepared from 0·5 gm. of potassium bromide, 10 cc. of 10 per cent. hydrobromic acid, and 90 cc. of water are added. The thalleioquin test is given by quinidine, cupreine, hydroquinine, and hydroquinidine, but not by cinchonine or cinchonidine. Morphine interferes with the formation of the colour, and various other substances, such as antipyrine and caffeine, have an effect on the test. The solution should, therefore, be as pure as possible when testing.

Tests.—Quinine forms characteristic crystals with sodium phosphate or potassium chromate solutions at 1 : 200 dilution. The picrate melts at 125° to 126° C. Quinine and its salts always contain a little cinchonidine and hydroquinine, and may also contain cinchonine or quinidine, but these latter are more likely to have been intentionally added.

Determination of Other Alkaloids.—A limit for cinchona alkaloids is fixed by the adoption by the B.P. and other pharmacopœias of the empirical test due to Kerner. According to the B.P. test as applied to quinine sulphate, 2 gm., after drying at 50° C., are digested at 60° to 65° C. in a stoppered tube with 20 cc. of water for half an hour, with repeated shaking, then cooled to 15° C. and kept at that temperature for half an hour, shaking from time to time. The crystals are filtered off on a small Buchner funnel or Gooch crucible at the pump and 5 cc. of the filtrate transferred to a dry test-tube and brought to 15° C. 6 cc. of 10 per cent. ammonia solution,

[1] *Amer. J. Pharm.*, 1912, **84**, 484; *J. Soc. Chem. Ind.*, 1921, **40**, 72T.

also at 15° C., are gradually added. The precipitate which forms should redissolve on rotating the tube, leaving no permanent precipitate in the liquid. Other pharmacopœias employ different amounts of ammonia solution—*e.g.* the U.S.P., 7 cc.; French Codex, 5 cc.; Dutch, 4·5 cc.; and German, 4 cc. Since 4·4 cc. is the amount required for pure quinine sulphate the last three standards are impracticable commercially, and that of the B.P. is difficult of attainment. The test is applied to the other salts of quinine by employing an amount of the salt equivalent to 2 gm. of the sulphate, neutralising if necessary with *N* sodium hydroxide, adding 1 gm. of sodium sulphate and making up to 20 cc. The test is then carried out as before. It is important in applying this test that the salts should be brought to the hydrogen-ion concentration of pure quinine sulphate before carrying it out, since the presence of free alkaloid has the same effect as impurities. The presence of even small amounts of inorganic salts impairs the value of the test, and in the case of salts of quinine other than the sulphate, the presence of the sodium sulphate used in the test decreases the solubility of the quinine sulphate, so that impure salts may be made to appear purer than they really are. Tutin,[1] therefore, concludes that the test is valueless for salts other than the sulphate.

Determination.—Quinine may be titrated with standard acid to the neutral salt using methyl red as an indicator, but the end-point is not sharp, and in order to obtain accurate results the titration should be carried to a standard colour corresponding to a solution of $pH=5{\cdot}6$. 1 cc. $N/10$ $HCl \equiv 0{\cdot}03783$ gm. quinine. Quinine may be determined in its salts by making the solution slightly alkaline with ammonia and extracting with chloroform in the usual way. After evaporating off the chloroform, the residue is dried at 115° C. and weighed as anhydrous quinine.

Quinine Bihydrobromide (Quinine Acid Hydrobromide), $C_{20}H_{24}O_2N_2.2HBr.3H_2O$. M.W.=540·2. (Anhydrous quinine, 60.)—It occurs as yellowish or white crystals, soluble in water, 14·2. The salt may be titrated with $N/10$ alkali to methyl red to $pH=5{\cdot}6$. 1 cc. $N/10$ $KOH \equiv 0{\cdot}054$ gm. quinine bihydrobromide.

Quinine Bihydrochloride (Quinine Acid Hydrochloride), $C_{20}H_{24}O_2N_2.2HCl$. M.W.=397·2. (Anhydrous quinine, 81·6.)—A white, crystalline powder, soluble in water, 133; in alcohol, 20; in chloroform, 14·3. It should not lose more than 3 per cent. at 100° C. Titration may be carried out as for the bihydrobromide. 1 cc. $N/10$ $KOH \equiv 0{\cdot}03972$ gm. quinine acid hydrochloride.

Quinine Bisulphate (Quinine Acid Sulphate), $C_{20}H_{24}O_2N_2.H_2SO_4.7H_2O$. M.W.=548·5. (Anhydrous quinine, 59·1; water, 26·6.)—Forms colourless or white, glistening crystals, efflorescing in dry air and becoming yellow on exposure to light; solubility in water, 10; in alcohol, 2. The salt should not lose more than 25 per cent. of its weight at 100° C., and should not leave more than 0·05 per cent. of ash on ignition. It may be titrated as for the bihydrobromide. 1 cc. $N/10$ $KOH \equiv 0{\cdot}05485$ gm. quinine bisulphate.

Quinine Citrate, $(C_{20}H_{24}O_2N_2)_2.C_6H_8O_7.3H_2O$. M.W=894·5. (Anhydrous quinine, 72·5.)—Forms white, acicular crystals. Soluble in water, 0·5; in alcohol, 2·2.

Quinine Ethylcarbonate (*Euquinine*), $C_2H_5CO_3.C_{20}H_{23}ON_2$. M.W.=396·3.

[1] *Amer. J. Pharm.*, 1912, **84**, 484.

(Anhydrous quinine, 81·8.)—White, light, almost tasteless, acicular crystals. Slightly soluble in water; readily soluble in alcohol, ether, or chloroform. M.Pt. 93° to 95° C.

Aristoquinine is quinine-carbonic ester; a white, almost tasteless powder, insoluble in water, and containing 96 per cent. of anhydrous quinine.

Quinine Glycerophosphate (*Kineurine*), $(C_{20}H_{24}O_2N_2)_2.C_3H_5(OH)_2.H_2PO_4.4H_2O$. M.W.=892·8. (Anhydrous quinine, 72·6; water, 8·07.)—Fine, white, crystalline needles. Slightly soluble in water and in alcohol, the solubility varying in different salts.

Determination of Phosphate.—0·1 gm. dissolved in 5 cc. of 25 per cent. nitric acid should give no appreciable precipitate on standing with 5 cc. of ammonium molybdate solution for an hour.

Quinine Hydrobromide, $C_{20}H_{24}O_2N_2.HBr.2H_2O$. M.W.=441·3. (Anhydrous quinine, 73·5; water, 8·16.)—Forms light, white, silky crystals. Soluble in water, 2·3 at 25° C.; very soluble in boiling water and in alcohol. The salt may be titrated with $N/10$ alkali to phenolphthalein. 1 cc. $N/10$ KOH ≡ 0·04413 gm. quinine hydrobromide.

Quinine Hydrochloride, $C_{20}H_{24}O_2N_2.HCl.2H_2O$. M.W.=396·8. (Anhydrous quinine, 81·7; water, 9·08.)—Forms white, silky crystals. Solubility in water, 3; in alcohol, 50; very soluble in chloroform. 1 gm. should dissolve completely in 7 cc. of a mixture of chloroform (2 vols.) and absolute alcohol (1 vol.). The water of crystallisation varies somewhat, but the salt should not lose more than 10 per cent. of its weight at 100° C. Titration may be carried out as for the hydrobromide. 1 cc. $N/10$ KOH ≡ 0·03968 gm. quinine hydrochloride. This salt should be tested for barium.

Quinine Hypophosphite, $C_{20}H_{24}O_2N_2.H_3PO_2$. M.W.=390·3. (Anhydrous quinine, 83·1; hypophosphorous acid, 16·9.)—A colourless, crystalline salt, slightly soluble in water and in alcohol.

Tests.—The hypophosphorous acid may be determined on the liquid remaining after the extraction of the quinine in the determination of the latter. The liquid is made slightly acid with hydrochloric acid, and an excess of mercuric chloride solution added. After standing for twenty-four hours in a warm, dark place, the precipitated mercurous chloride is filtered off through a Gooch crucible, washed, dried at 100° C., and weighed. $H_3PO_2=Hg_2Cl_2 \times 0{\cdot}1038$.

Quinine Lactate, $C_{20}H_{24}O_2N_2.C_3H_6O_3$. M.W.=414·3. (Anhydrous quinine, 78·38.)—Forms white needles resembling quinine sulphate. Solubility in water, 16; very soluble in alcohol.

Quinine Phosphate, $(C_{20}H_{24}O_2N_2)_3.2H_3PO_4.6H_2O$. M.W.=1277. (Anhydrous quinine, 76; water, 8·4); or $(C_{20}H_{24}N_2O_2)_2.H_3PO_4.8H_2O$. M.W.= 890·7. (Anhydrous quinine, 73; water, 16·2.)—This salt is of variable composition. It forms fine, white needles, slightly soluble in water and alcohol.

Quinine Salicylate, $C_{20}H_{24}O_2N_2.C_7H_6O_3.H_2O$. M.W.=480·4. (Anhydrous quinine, 87·5; salicylic acid, 28·7; water, 3·75.)—Forms white, silky crystals, very slightly soluble in water. Solubility in alcohol, 4; also soluble in chloroform.

Determination.—Dissolve 1 gm. in 50 cc. of $N/10$ hydrochloric acid in the presence of 25 cc. of ether. Separate, and further extract the salicylic acid with 25, 15, and 15 cc. of ether. Evaporate the ether at a low temperature and weigh the salicylic acid. Titrate the separated aqueous

solution with N/10 alkali to methyl red to a colour corresponding to $pH=5{\cdot}6$. 1 cc. $N/10$ HCl ≡ 0·04804 gm. quinine salicylate.

Quinine Sulphate, $(C_{20}H_{24}O_2N_2)_2.H_2SO_4.7\frac{1}{2}H_2O$. M.W. = 881·8. (Anhydrous quinine, 73·55; sulphuric acid, 11·1; water, 15·3.)—Forms small, light, white, silky crystals. Slightly soluble in water, 0·14; more soluble in dilute sulphuric acid, forming a solution with a blue fluorescence; soluble in alcohol, 1·5. 1 gm. should dissolve completely in 7 cc. of a mixture of chloroform (2 vols.) and absolute alcohol (1 vol.). The loss at 110° C. should not be more than 6·2 per cent., and the ash not more than 0·05 per cent. For the test for other cinchona alkaloids, see under Quinine. The most likely impurity in quinine sulphate is cinchonidine sulphate, which is present up to 2 or 3 per cent. in the best samples, while hydroquinine is also nearly always present.

Quinine Tannate.—A compound of quinine and tannic acid, containing from 30 to 35 per cent. of anhydrous quinine. It is a yellowish-white, tasteless powder, nearly insoluble in water, more soluble in alcohol. The ash should be inappreciable.

Quinine.—Mix 1 gm. with milk of lime, dry on the water bath, powder, and exhaust with chloroform. Evaporate off the chloroform and dry the residue at 115° C.

Quinine and Urea Hydrochloride, $C_{20}H_{24}O_2N_2.HCl.CO(NH_2)_2.HCl.5H_2O$. M.W.=547·3. (Contains anhydrous quinine, 59·2.)—Consists of white crystals. Solubility in water, 110 at 25° C.; in alcohol, 40 at 25° C.

Quinine Valerianate, $C_{20}H_{24}O_2N_2.C_5H_{10}O_2.H_2O$. M.W.=444·3. (Anhydrous quinine, 73.)—Colourless, lustrous, pearly crystals, with an odour of valerianic acid; slightly soluble in water, 1·2; in alcohol, 50.

Quinophan, B.P.C. (Cinchophen, U.S.P.). 2-Phenylquinoline-4-carboxylic acid; (*Agotan, Phenoquin,* or *Atophan*), $C_6H_5.C_9H_5N.COOH$. M.W.=249·2. —A white or yellowish powder, insoluble in water, but soluble in alkalis and hot alcohol. M.Pt. 209° to 211° C.

Determination.—Dissolve 0·5 gm. in 60 cc. of neutral alcohol by warming. Cool and titrate with $N/10$ sodium hydroxide to phenol red ($pH=7{\cdot}5$). 1 cc. $N/10$ alkali ≡ 0·0249 gm. quinophan. Quinophan may be extracted from acid solution with a mixture of equal volumes of ether and chloroform. For the determination as hydrobromide, see Palkin.[1]

Resorcin, $C_6H_4(OH)_2$. M.W.=110·1. (Resorcinol, *m*-Dihydroxybenzene.) —Forms colourless, glistening crystals, having a faint odour and pungent taste. M.Pt. 111° C. Solubility in water, 140; in alcohol, 200; readily soluble in glycerol.

Determination.—It may be determined in a similar manner to phenol by adding excess of an acidified standard solution of potassium bromide-bromate and titrating back the excess of bromine with $N/10$ thiosulphate solution after the addition of potassium iodide in excess.[2]

Tests.—It should leave no residue on ignition. The aqueous solution should be colourless and clear, and free from phenolic odour. It should not be more than slightly acid to litmus and should not be affected by the addition of lead acetate solution.

Saccharin (Gluside, *o*-Benzoyl sulphonimide), $C_6H_4.CO.SO_2.NH$. M.W. =183·1.—A white, crystalline powder, with an intensely sweet taste.

[1] *J. Amer. Pharm. Ass.*, 1927, **16**, 632.
[2] Rence, *J. Soc. Chem. Ind.*, 1911, **30**, 1369 (*cf.* Phenol, p. 163).

M.Pt. 219° to 222° C. Solubility in water, 0·4; in alcohol, 4; slightly soluble in ether or chloroform; readily dissolved by alkalis. 1 gm. should be completely soluble in 12 cc. of acetone at 16° C.

Tests.—1 gm., heated for four hours on a water bath with 10 cc. of a mixture of 4 vols. of sulphuric acid and 3 vols. of water, completely dissolves, and after dilution with an equal volume of water and allowing to stand twenty-four hours no crystals should separate (absence of *p*-benzoyl sulphonimide). The ash should be less than 0·1 per cent. Saccharin is a strong acid and may be titrated, but the figure obtained includes 1 : 4 sulphaminobenzoic acid, if present. 2 gm. should be dissolved in 25 cc. of *N*/2 NaOH and titrated back with *N*/2 HCl to phenol red. 1 cc. *N*/2 NaOH ≡ 0·0915 gm. saccharin. 1 cc. *N*/2 NaOH ≡ 0·1005 gm. 1 : 4 sulphaminobenzoic acid.

Determination.—Treat 0·6104 gm. of saccharin with 10 cc. of 7·5 *N* sodium hydroxide and boil for two minutes without undue concentration. Treat the product with 15 cc. of 10*N* hydrochloric acid and boil for thirty minutes under a reflux condenser. Sodium chloride should not be deposited during this boiling. Cool the solution, dilute with 75 cc. of water, and pass a current of air through the flask to remove any acid vapour. 15 cc. of 7·5 *N* sodium hydroxide are then added carefully and the ammonia distilled in the usual manner into 50 cc. of *N*/10 HCl. The number of cc. of acid neutralised × 3 = percentage of saccharin. Pure saccharin is known commercially as "*550*," which is intended to express its sweetness in terms of cane sugar. A less pure grade known as "*330*" is also sold. *Soluble saccharin* is the sodium salt of saccharin.

Saccharin Tablets. *Alkalinity.*—One tablet is added to 25 cc. of water, and when it has dissolved, 10 cc. of *N*/10 hydrochloric acid are added. The carbon dioxide is boiled off and the excess of acid titrated back with *N*/10 sodium hydroxide to phenol red. Let the number of cc. of *N*/10 acid used = x.

Determination.—Weigh 20 tablets into a 300 cc. Kjeldahl flask, add $25 + x$ cc. of 4*N* hydrochloric acid, and water to 50 cc. After boiling under a reflux condenser for one and a half hours, add 20 cc. of 7·5 *N* soda with a little powdered pumice and about 0·5 gm. of paraffin wax, and distil the ammonia into 50 cc. of *N*/10 acid. 1 cc. of *N*/10 HCl ≡ 0·0183 gm. saccharin. Number of cc. *N*/10 acid neutralised × 0·0141 = grains of saccharin per tablet.[1]

Safrol, $C_{10}H_{10}O_2$. M.W. = 162·1.—A colourless or yellow liquid having a sassafras-like odour. S.G. 1·09 to 1·106; refractive index (20° C.) about 1·538; optically inactive; B.Pt. 233° C. Safrol is the chief constituent of sassafras oil, but the commercial article is made by the fractionation of oil of camphor.

Salicin, $C_{13}H_{18}O_7$. M.W. = 286·2.—A glucoside occurring in various species of *Salix* and *Populus*, which on hydrolysis yields glucose and salicyl alcohol, $C_6H_4OH.CH_2OH$. It is a white, crystalline powder, having an extremely bitter taste. Soluble in water, 3·6; in alcohol, 1·2; insoluble in ether. M.Pt. 200° to 201° C.

Tests.—No residue should be obtained on ignition. The aqueous

[1] For further details concerning the testing of saccharin and saccharin tablets, see *J. Soc. Chem. Ind.*, 1918, **37**, 246T; *Analyst*, 1918, **43**, 402; *J. Soc. Chem. Ind.*, 1921, **40**, 150T; *J. Soc. Chem. Ind.*, 1919, **38**, 844A.

solution should be neutral to litmus, and should give no reaction with ferric chloride solution. It should give no precipitate with potassium iodide solution. 0·1 gm. warmed with 0·3 gm. of potassium dichromate and 2 cc. of dilute sulphuric acid gives an odour of salicylic aldehyde (meadowsweet).

Salicylic Acid, $C_6H_4OH\,.\,COOH$. M.W.=138·1.—Forms white, odourless, needle-shaped crystals. M.Pt. (when pure) 159° C. The lower limit of the B.P. range (156° to 159° C.) is too low. Good specimens should not melt below 157·5° C. Solubility in water, 0·18; more soluble in hot water; in alcohol, 49; very soluble in ether.

Determination.—Dissolve 0·3 gm. in 25 cc. of *N*/10 sodium hydroxide, and titrate back with *N*/10 hydrochloric acid to phenol red. 1 cc. *N*/10 NaOH ≡ 0·01381 gm. $C_6H_4OH.COOH$.

Tests.—Salicylic acid gives a deep violet colour with ferric chloride in neutral solution. This coloration is a delicate test for salicylic acid, and small amounts may be determined colorimetrically by this means.

Arsenic (B.P. Method).—Mix 5 gm. of salicylic acid with 2 gm. of lime and 5 cc. of water; dry and gently ignite. Dissolve the residue in 16 cc. of brominated hydrochloric acid and 45 cc. of warm water. Add stannous chloride solution, drop by drop, until colourless, and proceed as usual. Limit, 2 parts per million. The electrolytic method may be carried out directly.

Lead and *Tin.*—Estimated by the ordinary method on 7 gm., with 2 gm. in the control, solution being effected by means of dilute ammonia solution.

Salol (Phenyl Salicylate), $C_6H_4OH.COOC_6H_5$. M.W.=214·1.—Forms colourless, needle-shaped crystals with an aromatic odour. Nearly insoluble in water; soluble in alcohol, 18; very soluble in ether or chloroform. M.Pt. 42° to 43° C. Ash, inappreciable. No colour should be produced on shaking 1 gm. with 50 cc. of water, filtering, and testing the filtrate with 1 drop of ferric chloride solution. On boiling with sodium hydroxide solution and acidifying, an odour of phenol is developed and salicylic acid is precipitated. For the determination of salol in mixtures with phenacetin or acetanilide, see Emery.[1]

Santonin, $C_{15}H_{18}O_3$. M.W.=246·1.—Small, white, shining, odourless crystals. Insoluble in water; solubility in alcohol, 2; in ether, 0·7; in chloroform, 40; insoluble in dilute acids. M.Pt. 170° C. Santonin becomes yellow on exposure to sunlight. A red-violet colour is formed with alcoholic potash. (For the determination of santonin, see p. 219.)

Scarlet Red, Medicinal. (Benzene-azo-benzene-azo-β-naphthol; formerly toluene-azo-toluene-azo-β-naphthol (Biebrich Scarlet R.) was used. M.Pt. 185° C.)—Scarlet red is a red powder; insoluble in water; soluble in alcohol and ether. M.Pt. 195° C. Ash, nil. It forms a bluish-green solution in conc. sulphuric acid.

Sparteine Sulphate, $C_{15}H_{26}N_2.H_2SO_4.5H_2O$. M.W.=422·4.—A white, crystalline powder, or forms colourless, hygroscopic crystals. Solubility in water, 200; in alcohol, 20. Loss at 100° C. 21·3 per cent. M.Pt. (anhydrous) 150° to 152° C.

Tests.—To 0·1 gm. in a test-tube add 25 cc. of ether and a few drops of 1 per cent. ammonia solution. Add an ethereal solution of iodine

[1] *J. Ind. Eng. Chem.*, 1921, 13, 539.

(1 in 50) until the liquid, when shaken, turns from an orange to a dark reddish-brown colour. After a short time the bottom and sides of the test-tube will be coated with minute dark greenish-brown crystals. A 10 per cent. aqueous solution gives with sodium hydroxide solution a white precipitate, which soon becomes united into oily drops, which are soluble in ether and chloroform.

Starch.—Various starches are used for different purposes in pharmacy. The analysis of all of them involves microscopic examination, ash, acidity, and moisture determinations. The reaction is tested by shaking 1 gm. with 10 cc. of neutral distilled water, and roughly determining the *p*H value by means of a suitable indicator. Most starches are faintly acid, but rice starch is sometimes alkaline. The B.P. requires that cold water, mixed with an equal weight of starch, shall not become more than faintly acid or alkaline to litmus. Air-dried starch usually contains from 12 to 20 per cent. of moisture. Starch is insoluble in cold water, but in hot water swells up and forms a gelatinous liquid.

Arrowroot (Varieties: St. Vincent, Natal, and the so-called Bermuda). —A white, practically odourless powder. On making a paste of 10 gm. in 100 cc. of boiling water no objectionable odour or taste should be observed. Ash, not more than 0·2 per cent.

Maize, Rice, and Wheat Starches.—White, odourless powders. Ash, not more than 0·2 per cent. The Public Health (Preservatives, etc. in Food) Regulations prohibit the presence of more than 100 parts per million of sulphur dioxide in starch.

Stearic Acid, $C_{18}H_{36}O_2$. M.W.=284·4.—Pure stearic acid is a white, crystalline solid with a greasy feel. Insoluble in water; soluble in alcohol, 1·6; readily soluble in ether; only slightly soluble in petroleum ether. M.Pt. 69·3° C. Commercial stearic acid (" stearine ") is a mixture of solid fatty acids. For pharmaceutical purposes the M.Pt. should not be below 56° C. Acid value, 200 to 210. Saponification value, 200 to 220. 1 cc. *N*/10 NaOH ≡ 0·02844 gm. stearic acid. The alcoholic solution should not give a red or orange colour with thymol blue (absence of mineral acid).

Strophanthin.—A glucoside or mixture of glucosides derived from the seed of *Strophanthus Kombé* or other species of *Strophanthus*. It is a white or pale yellow powder; soluble in water (2·5) and alcohol; insoluble in ether or chloroform. Sulphuric acid containing one-fifth of its volume of water gives a green colour with strophanthin changing to brown. If a few crystals of resorcinol and then a few of strophanthin are added to 4 or 5 cc. of conc. hydrochloric acid, and the latter heated to 60° or 70° C. in a water bath for a few minutes, a pink coloration appears.

Ouabain, sometimes erroneously called crystallised strophanthin or *g*-strophanthin, is obtained from the wood of *Acocanthera Schimperi* or from the seeds of *Strophanthus gratus*. It is a white, crystalline powder, soluble in water, 0·7. Ouabain gives no colour with the above resorcinol test.

Strychnine, $C_{21}H_{22}O_2N_2$. M.W.=334·2.—Forms translucent, colourless prisms, or a white, crystalline powder. M.Pt. 265° to 266° C. Solubility in water, 0·014; in alcohol, 0·59; in chloroform, 10·2 at 25° C.; in ether, 0·04; practically insoluble in petroleum ether. The aqueous solution is extremely bitter in taste, noticeable in a dilution of 1 : 700,000.

Determination.—Dissolve 0·6 gm. in 25 cc. of *N*/10 hydrochloric acid,

and titrate back with $N/10$ sodium hydroxide to methyl red to an ora colour (pH=5·0). 1 cc. $N/10$ HCl ≡ 0·03342 gm. strychnine.

Tests.—Sulphuric acid containing 1 per cent. of ammonium vanadate gives a deep violet-blue colour, changing to a deep purple on standing, and on dilution with water to a cherry red. A similar colour is produced by dissolving a crystal in a drop of sulphuric acid on a plate, and adding a small crystal of potassium dichromate. Yohimbine gives an almost identical colour. The presence of brucine may be detected by dissolving 0·2 gm. in 2 cc. of dilute nitric acid (1 : 1); the colour formed should be yellow, not red. Ash, negligible. Strychnine forms characteristic crystalline precipitates with gold chloride at 1 : 1000 or greater dilutions, and with chromic acid at about 1 : 2000 dilutions. These are the most characteristic precipitates, but crystalline precipitates are also formed with numerous other reagents.

Strychnine Hydrochloride, $C_{21}H_{22}O_2N_2.HCl.2H_2O$. M.W.=406·8. (Strychnine, 82·1; water, 8·85.)—The water of crystallisation more often corresponds to $1\frac{1}{2}H_2O$ (strychnine, 84; water, 6·79). Small, colourless crystals. Solubility in water, 2·86; in alcohol, 1·37; in chloroform, 0·59. Loss in weight at 110° C., 7 to 9 per cent.

Brucine.—See Strychnine.

Strychnine Nitrate, $C_{21}H_{22}O_2N_2.HNO_3$. M.W.=397·2. (Strychnine, 84·1.) —Colourless, glistening crystals. Solubility in water, 1·4; in alcohol, 0·8. For other tests, see Strychnine.

Strychnine Sulphate, $(C_{21}H_{22}O_2N_2)_2.H_2SO_4.5H_2O$. M.W.=856·7. (Strychnine, 78; water, 10·5.)—Colourless crystals. Solubility in water, 2; in alcohol, 0·7. Loss in weight at 100° C., not more than 11 per cent. For other tests, see Strychnine.

Succinic Acid, $(CH_2COOH)_2$. M.W.=118·1.—Colourless prisms. Solubility in water, 5; in alcohol, 7·5; in ether, 1·26. M.Pt. 155° C. On gently warming with sulphuric acid no charring should take place. It may be determined by titrating 0·15 gm. with $N/10$ sodium hydroxide solution to thymol blue to a blue colour. 1 cc. $N/10$ NaOH ≡ 0·005905 gm. $(CH_2COOH)_2$.

Sucrose, $C_{12}H_{22}O_{11}$. M.W.=342·2.—Solubility in water, 190 at 10° C. Practically insoluble in alcohol. M.Pt. 160° C. $[\alpha]_D=+66·5°$.

Tests.—Should be free or practically free from ash, moisture, chlorides, sulphates, and reducing sugars.

Determination.—By the polarimeter.

Sulphanilic Acid, $C_6H_4.NH_2(1).SO_3H(4).2H_2O$. M.W. = 209·2.—Colourless crystals. Soluble in water, 0·9; insoluble in alcohol, ether, or chloroform. It decomposes at 300° C. with no definite M.Pt. It may be determined by titrating 0·5 gm. with $N/10$ sodium hydroxide to thymol blue (1 cc. $N/10$ NaOH ≡ 0·02092 gm. sulphanilic acid), or by treating 0·5 gm. with 200 cc. of a 5 per cent. hydrochloric acid solution, and titrating with $N/10$ potassium nitrite solution until potassium iodide-starch is changed to a permanent blue. 1 cc. $N/10$ KNO_2 ≡ 0·02092 gm. sulphanilic acid.

Sulphonal (Sulphonemethane. Dimethylmethane-diethylsulphone), $(CH_3)_2C.(SO_2C_2H_5)_2$. M.W.=228·3.—Colourless, odourless crystals. M.Pt. 125° C. Solubility in water, 0·22; in alcohol, 1·25; in ether, 0·8.

Tests.—Sulphonal dissolves in sulphuric acid, forming a solution from which the sulphonal is precipitated on the addition of water. The ash

should be negligible. When heated with an equal weight of potassium cyanide the odour of mercaptan is evolved, and when to the solution of the product in water excess of hydrochloric acid and a few drops of ferric chloride are added, a reddish colour is developed. Sulphonal should give no reaction for chlorides and sulphates.

Tannic Acid (Gallotannic Acid).—A light, yellowish or brownish powder, with a faint, characteristic odour. Solubility in water, 100; in alcohol, 100; slowly soluble in glycerin, 33; almost insoluble in ether or chloroform.

Tests.—Ash, not more than 0·2 per cent. A red coloration on the addition of potassium cyanide solution indicates the presence of gallic acid, which reduces the solubility of the acid. If necessary, gallic acid may be determined by the method of Dreaper.[1] An aqueous solution of tannic acid precipitates albumin or antimony potassium tartrate solution.[2]

Tartaric Acid, $C_4H_6O_6$. M.W.=150·1.—Forms large, transparent crystals. Solubility in water, 140; in alcohol, 40; slightly soluble in ether, 0·4. Ash, not more than 0·1 per cent.

Determination.—Dissolve 1 gm. in 25 cc. of water, add 25 cc. of *N*/2 sodium hydroxide from a pipette, and continue the titration to phenol red until red. 1 cc. *N*/2 NaOH ≡ 0·03751 gm. $C_4H_6O_6$. The B.P. requires not less than 98 per cent.; U.S.P. 99·5 per cent.

Determination of Arsenic.—By the general method on 7 gm.; B.P. limit, 1·4 parts per million.

Lead.—By the general method on 7 gm., with 2 gm. in the control, solution being effected by means of ammonia. (2 gm. require 6 cc. of 10 per cent. ammonia.) B.P. limit, 20 parts per million.

Sulphate.—2·5 gm. dissolved in 50 cc. of water, on the addition of 5 cc. of barium chloride solution with immediate mixing should not yield a greater opalescence than 0·5 cc. of *N*/20 sulphuric acid in 50 cc. of water under the same conditions.

Terebene.—A mixture of dipentene and other hydrocarbons obtained by shaking oil of turpentine with sulphuric acid and distilling. A colourless liquid of pleasant odour. S.G. 0·854 to 0·862.

Boiling Range.—Not more than 5 per cent. distils below 160° C., the main fraction coming over between 165° and 185° C., leaving only a slight residue. The B.P. standards are not practicable.

Terpin Hydrate, $C_{10}H_{18}(OH)_2.H_2O$. M.W.=190·2.—Colourless, glistening, rhombic prisms. M.Pt. 116° to 117° C. if quickly heated. Solubility in water, 0·4; in alcohol, 7; slightly soluble in ether or chloroform. Ash, nil. When a few drops of sulphuric acid are added to the hot aqueous solution the liquid becomes turbid and acquires the pleasant odour of terpineol.

Theobromine (Dimethylxanthine), $C_5H_2(CH_3)_2O_2N_4$. M.W.=180·1.—A white, crystalline, odourless powder containing 31·1 per cent. of nitrogen. Sublimes at 290° C. Solubility in water, 0·05; in alcohol, 0·2 (Caffeine has solubility 2·5); only slightly soluble in ether and chloroform; soluble in sodium hydroxide solution.

Tests.—The ash should be negligible. The solution gives no precipitate with Mayer's reagent or picric acid.

Determination of Caffeine.—If 1 gm. is mixed with 4 cc. of water, and

[1] *J. Soc. Chem. Ind.*, 1893, **48**, 2.
[2] *Cf.* Mitchell, *Analyst*, 1923, **48**, 2.

sufficient sodium hydroxide solution added to dissolve it, and then tl solution is shaken with 10 cc. of chloroform, the latter on evaporation shoul not leave a residue of more than 6 milligrams (absence of caffeine).

Theophylline is also a dimethylxanthine. *Theocin* is synthetic the phylline.

Theobromine Sodium Sodio-Acetate (*Agurin*), $C_7H_7N_4O_2Na.NaC_2H_3O$ M.W.=284·1. (Theobromine, 63·3.)—A white, deliquescent powder, readil soluble in water, 50.

Theobromine Sodium Salicylate (*Diuretin*), $C_7H_7O_2N_4Na.NaC_7H_5O$ M.W.=362·2. (Theobromine, 49·8; salicylic acid, 38·1.)—A white, odou less, amorphous powder. The compound is unstable, and becomes le soluble on keeping. Solubility in water, 100; soluble in alcohol; ir soluble in ether or chloroform.

Determination of Theobromine.—Dissolve 2 gm. in 10 cc. of warm wate and titrate with *N* hydrochloric acid to thymol blue—not more tha 5·5 cc. should be required. Add one or two drops of 2 per cent. ammoni solution. Allow to stand at 20° to 25° C. for three hours, filter throug a tared 9 cm. filter or Gooch crucible, and wash with four quantities of 5 c.c of water at 0° C. Dry at 100° C., and weigh. Add 0·13 gm. to the weigh to correct for solubility. Not less than 46·5 per cent. theobromine shoul be present (U.S.P.). The B.P. requires not less than 40 per cent., but doe not add a correction.

Salicylic Acid may be determined by acidifying the filtrate from th above with hydrochloric acid, shaking out with 20, 10, and 10 cc. of ethe drying the residue at a low temperature and weighing. The B.P. require not less than 35 per cent.

Caffeine.—Dissolve 1 gm. in 10 cc. of water and a few cc. of sodiun hydroxide solution. Extract with 10 cc. of chloroform. The residue fron the chloroform should weigh not more than 0·005 gm.

Thiosinamine (Allyl-thiourea), $CS(NH_2)NHC_3H_5$. M.W.=116·1.—White glistening crystals, sometimes having a faint odour of mustard oil. Solu bility in water, 6; in alcohol, 50; also soluble in ether. M.Pt. 74° C. Th aqueous solution gives a white precipitate with mercuric salts or silve nitrate.

Thiosinamine Sodium Salicylate (*Fibrolysin*).—This salt is more solubl in water than thiosinamine.

Thiosinamine Ethyl Iodide (*Iodolysin*).—Contains 43 per cent. thiosin amine and 47 per cent. iodine. It is readily soluble in water.

Thymol, $C_{10}H_{13}OH$. M.W.=150·1.—Forms large, colourless crystal having an odour of thyme. M.Pt. 50° to 51° C.; B.Pt. 232° C.; S.G. 1·02 Solubility in water, 0·07; very soluble in alcohol, ether, or chloroform.

Determination.—Dissolve 0·25 gm. in sodium hydroxide solution, ad 100 cc. of *N*/10 iodine solution, acidify with sulphuric acid, filter, an titrate the excess of iodine with *N*/10 thiosulphate solution. 1 cc. *N*/1 I ≡ 0·00375 gm. thymol.

Tests.—The ash should be negligible. The alcoholic solution should no give a blue colour with dilute ferric chloride solution.

Thymol Iodide (Dithymol di-iodide), $C_{20}H_{24}O_2I_2$. M.W.=550·1.—Red dish-brown powder with a slight aromatic odour, containing 46·1 per cent of iodine. Insoluble in water or alcohol; soluble in ether or chloroform, 10 leaving a slight residue.

Determination.—Mix 0·15 gm. with 3 gm. of anhydrous sodium carbonate and heat gradually until completely charred. Extract with hot water, filter, and wash until free from iodide. Heat the combined washings and add potassium permanganate solution until pink. Remove the pink colour with just sufficient alcohol, cool, and dilute to 200 cc. Filter, rejecting the first 50 cc. of filtrate. To 100 cc. of the clear filtrate add 1 gm. of potassium iodide and excess of dilute sulphuric acid. Titrate the liberated iodine with *N*/10 thiosulphate. 1 cc. *N*/10 $Na_2S_2O_3 \equiv 0{\cdot}002115$ gm. I. Not less than 40 per cent. should be present.

Tests.—Ash not more than 1·5 per cent. On shaking 0·4 gm. with 10 cc. of water and filtering, the solution should not give a reaction for free iodine or iodide.

Toluene, $C_6H_5CH_3$. M.W.=92·1.—A colourless, light, highly refractive liquid, insoluble in water; miscible with alcohol, ether, or chloroform. B.Pt. 110° to 112° C.; S.G. 0·872.

Trichloracetic Acid, CCl_3COOH. M.W.=163·4.—Colourless, deliquescent crystals with a pungent odour, very soluble in water, alcohol, or ether. M.Pt. about 55° C.; B.Pt. 195° C. Chloride should be absent from the freshly prepared solution. The acid may be determined by dissolving 2 gm. in 50 cc. of water and titrating with *N*/2 sodium hydroxide to thymol blue. 1 cc. *N*/2 $NaOH \equiv 0{\cdot}08169$ gm. trichloracetic acid.

Uradal (*Adalin*; Bromodiethylacetylurea), $(C_2H_5)_2.CBr.CO.NH.CO.NH_2$. M.W.=237·1. (Bromine, 33·7; nitrogen, 11·8.)—A white, odourless, crystalline powder, slightly soluble in cold water, soluble in boiling water, alcohol, or chloroform. M.Pt. 115° to 116° C. On hydrolysis with alkalis, urea and bromodiethyl-acetic acid are formed.

Uvaleral (*Dormigene* or *Bromural*; α-Bromo*iso*valerylurea), $(CH_3)_2.CH.CHBr.CO.NH.CO.NH_2$. M.W.=223·0. (Bromine, 35·7; nitrogen, 12·5.)—Forms white crystals with a faint valerian odour, slightly soluble in cold water; soluble in hot water, alcohol, or ether. M.Pt. 145° to 146° C. On hydrolysis with alkalis, urea and α-bromo*iso*valeric acid are formed.

Urea, $CO(NH_2)_2$. M.W.=60·0.—Colourless, transparent crystals; solubility in water, 70; in alcohol, 14; insoluble in ether or chloroform. The substance contains 46·6 per cent. of nitrogen. M.Pt. 132° to 133° C.

Urethane (Ethyl Carbamate), $C_3H_7O_2N$. M.W.=89·1. (Nitrogen, 15·7.)—Forms colourless, prismatic crystals. Soluble in water, 74·2; very soluble in alcohol, ether, or chloroform. M.Pt. 48·5° C. An aqueous solution (1 in 1) should not give a precipitate with nitric or oxalic acids, or with mercuric nitrate solution (absence of urea).

Valerianic Acid (Valeric acid), $C_5H_{10}O_2$. M.W.=102·1.—The commercial product, and that occurring in valerian root, is the *iso*-compound. A colourless liquid with an objectionable and persistent odour. Soluble in water, 3; readily miscible with alcohol or ether. S.G. 0·937; B.Pt. 175° C. It forms a hydrate, $C_5H_{10}O_2.H_2O$ boiling at 165° C., but this is gradually dehydrated on distillation.

Determination.—Valeric acid may be titrated with *N*/2 alkali to thymol blue to the neutral green tint. 1 cc. *N*/2 $NaOH \equiv 0{\cdot}05105$ gm. Valeric acid.

Vanillin (Vanillic aldehyde), $C_8H_8O_3$. M.W.=152·1.—The flavouring principle of vanilla. It forms white, crystalline needles with an intense odour

of vanilla. Slightly soluble in water, 1; more easily soluble in boiling water; very soluble in alcohol or ether. The ash should be negligible. M.Pt. 80° to 81° C.

Tests.—If vanillin is warmed with concentrated alcoholic sodium hydroxide and chloroform is added, no odour of phenyl *iso*nitrile should be developed (absence of acetanilide). If vanillin with twice its weight of phloroglucin is dissolved in alcohol and a little hydrochloric acid is added to the solution, a fiery red coloration will be produced on evaporating the liquid.

Veratrine.—A mixture of alkaloids—cevadine, veratridine, sebadine, sabadinine, etc., obtained from sabadilla. The U.S.P. IX preparation is from *Asagræa officinalis*. Consists of white or greyish-white pulverulent masses which are amorphous, odourless, and slightly hygroscopic. Almost insoluble in water; solubility in alcohol, 33; in ether, 6; in chloroform, 33. M.Pt. (indefinite) 145° to 155° C.

Xylene, C_8H_{10}. M.W.=106·1.—A colourless liquid of peculiar odour, insoluble in water. S.G. 0·857 to 0·866. Boiling range, 136° to 142° C. For other tests, see Benzene, p. 132.

PART IV.

CRUDE DRUGS.

SECTION I.

VEGETABLE DRUGS.

Sampling.—Proper sampling is a matter of some difficulty. It is equally as important as accurate analysis, for unless the former has been carried out satisfactorily, obviously the latter is of no avail.

It is not always an easy matter to ensure that a sample is really representative of the bulk. Wherever possible, a sample from each package should be examined separately. The sample should be taken from the middle of the materials or, at any rate, the outer portion should be removed. If possible, the contents should be mixed, or samples should be taken from different parts of the parcel and mixed, afterwards taking a portion of this mixture for analysis. Some materials require special treatment, *e.g.* opium (*q.v.*).

If each package of a consignment cannot be examined separately it is usual to take samples from each package, mix them, and draw a sample from this for examination. This is open to the objection that the bad quality of one package may be so diluted by the good quality of the rest of the packages that it is overlooked altogether, but any material which differs in appearance from the rest of the consignment should be sampled separately. Composite samples of large bulk are treated by the process known as "quartering," in order to reduce them to the size of a working sample. This is done by thoroughly mixing the composite sample and dividing into four equal portions. One of these quarters is taken and again divided into four parts, and so on until one quarter is reduced to working size. If only a small sample has been received for analysis it is advisable, if it is not uniform, to grind the greater part of it to powder, and mix thoroughly before analysis, keeping a small representative part unground for reference. It often happens that grinding is not possible, and in that case it is better to divide up the sample into a number of equal portions, each as far as possible representative of the whole sample; one or two of these portions should then be used for each analytical operation.

Moisture.—This determination is usually carried out by weighing out about 2 gm. of the powdered drug into a flat dish and heating at the temperature of the steam oven (about 95° to 98° C.) until constant weight is attained. This method will fail where volatile oil is present, and it is then necessary to determine the moisture by one of the following methods :—

The Calcium Carbide Method.[1]—Half a gram of the finely powdered drug is introduced into a stout tube, 5 by ⅝ in., dried sand added to a depth of about ¾ in., and then calcium carbide in moderately large pieces to within 1½ in. of the mouth of the tube, which is connected to a calcium chloride tube, and this to a brine-filled nitrometer. The tube containing the drug is immersed in a brine bath, to the upper level of the carbide, and after the apparatus has been adjusted to atmospheric pressure, the bath is gradually heated and finally boiled, the boiling being continued until the volume of gas ceases to increase during five minutes. The process usually takes about one and a half hours. After cooling and adjusting the pressure, the volume of gas is read and calculated to N.T.P.

Then: Number of cc.×0·001725=weight of water in the quantity of drug taken. The acetylene should not be allowed to stand over the brine for any length of time before reading the volume.

The Toluene Method.[2]—The apparatus (fig. 16) consists of a 250 cc. flask, A, connected by means of a "distilling tube receiver" with a straight Liebig's condenser. The tube, B, is graduated in tenths of a cc. The whole apparatus should be kept thoroughly clean by means of chromic acid mixture in order to prevent drops of water from adhering to the sides of the tube. The determination is carried out by introducing about 75 cc. of pure toluene into the flask; if the liquid is inclined to bump or char, some pieces of porous pot or a layer of sand should be added. Sufficient of the sample to give about 2·5 cc. of water is then added and the apparatus is connected up. Distillation is carried on until no further sign of condensed water is seen. Any drops adhering to the sides of the condenser or tube may be pushed down by a coil of thin copper wire. The volume of water in the tube at 15° C. is then read off and the percentage calculated.

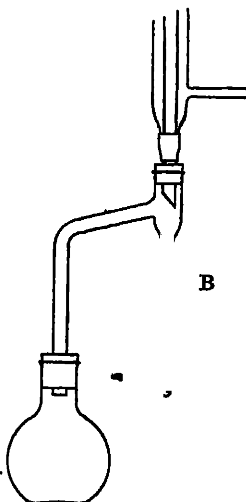


FIG. 16.—Apparatus for Moisture Determination.

Mineral Matter.—About 2 gm. are accurately weighed into a platinum or silica dish and ignited, gently at first, over an Argand burner. The temperature should not rise above a low red heat. In some cases, where it is difficult to remove carbon, moistening the ash with a little ammonium nitrate solution and again cautiously igniting will help. When the ash is free from carbon it is cooled in a desiccator and weighed.

Mineral Matter Insoluble in Hydrochloric Acid.—The ash of the majority of drugs is soluble to a large extent in hydrochloric acid. Any excess of insoluble ash will therefore indicate the presence of extraneous material, possibly in the form of adhering earthy matter, or deliberately added.

The ash obtained as above is warmed with dilute hydrochloric acid, which is decanted off through an ashless filter paper or Gooch crucible; the treatment is repeated and the insoluble matter then washed on to the filter paper, which is ignited in a platinum dish and the insoluble matter weighed.

[1] Dupré, *Analyst*, 1906, **31**, 213; Cripps and Brown, *ibid.*, 1909, **34**, 519.
[2] See Jones and McLachlan, *Analyst*, 1927, **42**, 383.

Matter Insoluble in Alcohol.—2 gm. of the finely powdered drug are treated in a beaker with 50 cc. of alcohol of the required strength, covered with a watch-glass and warmed (unless the determination is being carried out in the cold). After standing for the required time with the alcohol, with occasional stirring, the liquid is decanted through a weighed Soxhlet tube (fig. 17) containing a small plug of pure cotton- or glass-wool and fixed in a flask connected to a filter pump. The residue is treated with two further quantities of alcohol and finally washed with alcohol into the Soxhlet tube, which is dried in the oven until constant in weight. Some drugs, *e.g.* those containing tannin, rapidly clog a filter and then are extremely slow in filtering; the use of the Soxhlet tube greatly shortens the time of filtration in these cases.

Matter Soluble in Alcohol.—5 gm. of the finely powdered drug are shaken with 50 cc. of alcohol of the required strength in a stoppered separator with a small plug of cotton pushed firmly down just above the top of the tap, and allowed to stand overnight. The alcohol is then run into a stoppered cylinder and further alcohol allowed to percolate slowly through the drug until the percolate measures 100 cc.; 10 cc. of the latter are then evaporated to dryness and the residue weighed, the soluble matter being calculated as a percentage of the drug.


Fig. 17. Soxhlet Tube.

Matter Soluble in Water.—Proceed as above, using water instead of alcohol.

Ether Extract.—2 gm. of the dry powder are weighed into a Soxhlet thimble and extracted in a continuous extraction apparatus with dry ether until exhausted If the drug contains volatile oil the ether is partly distilled off at a low temperature and the remainder allowed to evaporate spontaneously The residue is dried in a desiccator over sulphuric acid and weighed, =total ether extract. The volatile oil is then driven off by heating at 100° C. until constant in weight; the residue is weighed as non-volatile ether extract. The difference gives the amount of "volatile ether extract." If the drug contains no volatile oil, the ether is distilled off and the residue dried at 110° C. and weighed.

Crude Fibre.—2 gm. of the dry, fat-free, powdered drug are weighed into a 500 cc. flask, and 200 cc. of boiling 1·25 per cent. sulphuric acid added. The liquid is kept boiling for half an hour under a reflux condenser. It is then filtered through a circle of calico on the bottom of a Gooch crucible and washed with boiling water until the washings are no longer acid. The residue is washed back into the flask with 200 cc. of boiling 1·25 per cent. sodium hydroxide solution. Then the mixture is again boiled for half an hour under a reflux condenser, filtered rapidly through a Gooch crucible containing asbestos, washed with boiling distilled water until no longer alkaline, dried at 110° C., and weighed. The crucible is ignited and weighed again. The difference represents the crude fibre in the weight taken.

Volatile Oil.—Apart from the volatile ether-soluble extract given above, the volatile oil may also be determined as follows:[1] The total volatile matter is determined by heating about 2 gm. in a tube through which a current of dry air is aspirated in an air-bath at 135° C. In about an hour all the volatile matter is removed. The moisture is then determined by

[1] Cripps and Brown, *Analyst*, 1909, **34**, 519.

the toluene method (see p. 179) and subtracted from the result. If larger quantities of material are available, or if the percentage of volatile oil is high, as in copaiba, the oil may be determined by distillation with steam, or *in vacuo*.

The P.G. method for determining volatile oil is, in essentials, as follows: 10 gm. of the drug, in the form of coarse powder, are introduced into a round-bottomed flask of 1 litre capacity with 300 cc. of water and distilled over wire gauze into a flask or separator of 300 cc. capacity, marked at 150 and 200 cc. As soon as 150 cc. have been collected the flame is removed temporarily, and when the boiling ceases the flask is carefully rotated so as to wash the material from the walls back into the liquid. Then the boiling is continued until a further 50 cc. have passed over. The distillate is placed in a separator with 60 gm. of sodium chloride and the solution shaken three times with 20 cc. of pentane. The united extracts are allowed to stand for some minutes and then transferred to a wide-necked tared flask of 100 cc. capacity, taking precautions to prevent any of the salt solution from getting into the flask. The pentane is carefully distilled off on a moderately heated water bath. The last portion of the solvent is separated by a very gentle blast of dry air. The flask is placed in a desiccator for half an hour and weighed. It is then returned to the desiccator and kept therein until the weight does not differ by more than 0·002 gm. in a quarter of an hour.

ALKALOIDS.

General Method of Determination: Keller's Method.—From 10 to 25 gm. of the finely powdered drug are placed in a flask with a measured quantity of ether-chloroform (3 : 1). Enough of the solvent should be used to cover the drug completely. The mixture is shaken occasionally during ten minutes. 3 cc. of ammonia solution (10 per cent.) are then added and the shaking continued occasionally for thirty minutes. A little water is then added and the mixture shaken until the drug runs together and the solvent is clear. An aliquot part of the solvent is then measured into a separator and shaken with 25, 15, and 10 cc. of 0·5 to 1·0 per cent. hydrochloric acid, the acid solutions being run off into a second separator. A slight excess of dilute ammonia solution is added to the acid liquid and the liberated alkaloids extracted by shaking with three successive portions of a mixture of equal parts of ether and chloroform. The ether-chloroform solution is run through a small filter paper into a tared flask, the solvent distilled off, and the residue dried for thirty minutes at 100° C. and weighed. It is then dissolved in 5 to 10 cc. alcohol and titrated with *N*/20 hydrochloric acid, using methyl red as an indicator.

In the determination of alkaloids the following precautions must be taken in order to obtain reliable results:

1. Solutions which have been extracted with volatile solvents should be tested with Mayer's reagent (potassium-mercuric iodide) to ensure that no alkaloids remain unextracted.

2. After running off a volatile solvent the stem of the separator should be rinsed out by allowing a few drops of the next quantity of solvent added to run through before shaking.

3. The outside of the stem of the separator should be rinsed down with a few drops of the solvent after the extraction is complete.

4. Care should be taken to avoid the formation of emulsions. This may be avoided or mitigated by—

(*a*) using a larger volume of solvent;

(*b*) avoiding violent shaking;

(*c*) making the solution more strongly acid or alkaline.

Emulsions, once formed, may sometimes be broken up by adding a small tuft of cotton-wool and stirring with a glass rod, or by the addition of a few drops of alcohol. In the case of very troublesome emulsions it is best to evaporate down with a little dilute acid until the solvent is removed, filter the acid solution, redissolve the residue in the solvent and again evaporate down with acid, filtering off the acid as before. This should be continued until no more alkaloid is extracted.

5. Alkaloids should not be dried at temperatures above those laid down in the methods used.

6. Where alkaloids are easily hydrolysed (*e.g.* atropine) the process should be carried through as rapidly as possible. Prolonged contact with alkali should be avoided.

Care should be taken to see that the separators used, which should be pear-shaped, have well-fitting stoppers and taps which do not leak. The stems should be cut off diagonally and as short as possible. The separators are conveniently arranged in batteries on a wooden stand provided with holes to take them (fig. 18).

Aconite.—Aconite is the dried root of *Aconitum Napellus*. The most important constituent is aconitine (see p. 126). The usual methods of standardisation, however, are based on the separation of ether-soluble alkaloids, which are composed of other alkaloids as well as aconitine. There is no method available for the accurate determination of aconitine alone. Aconitine is readily hydrolysed, and precautions must be taken to prevent this during the alkaloidal determination.

The B.P. gives the following process for the determination of ether-soluble alkaloids: Into a small, stoppered, glass percolator, provided with a glass tap and suitably plugged with cotton-wool, introduce 10 gm. of aconite root in No. 40 powder and 75 cc. of alcohol (70 per cent.). Macerate for four hours, shaking occasionally. Then allow the percolation to proceed slowly until the liquid ceases to drop. Continue the percolation by the addition of more of the same menstruum until 150 cc. have been collected or the root is exhausted. Evaporate the percolate to dryness in a shallow porcelain evaporating basin, at a temperature not exceeding 60° C. Dissolve the residue in 5 cc. of *N*/10 solution of sulphuric acid diluted with 20 cc. of water. Filter into a separating funnel, washing the dish and filter with about 30 cc. of water. Add to the mixed filtrate and washings 25 cc. of ether and 2 cc. of solution of ammonia, and shake for one minute. After separation draw off the lower layer into a flask and filter the ethereal solution into a beaker. Return the contents of the flask to the separator, add 20 cc. of ether and again shake for one minute, separating the aqueous liquid and filtering the ethereal solution into the beaker. Repeat the operation with two other portions each of 20 cc. of ether. Evaporate the mixed ethereal solutions to dryness, dry the residue at 60° C., dissolve it in 5 cc. of *N*/20 solution of sulphuric acid diluted with 20 cc. of water, and titrate back with *N*/20 solution of sodium hydroxide, tincture of cochineal being used as indicator. Deduct the number of cc. of the alkaline solution

required from 5. Each cc. of the difference corresponds to 0·03217 gm. of ether-soluble alkaloids. The U.S.P. has abandoned a chemical standard for aconite and substitutes a physiological assay.

Agar or **Agar Agar** is the dried mucilaginous substance extracted from

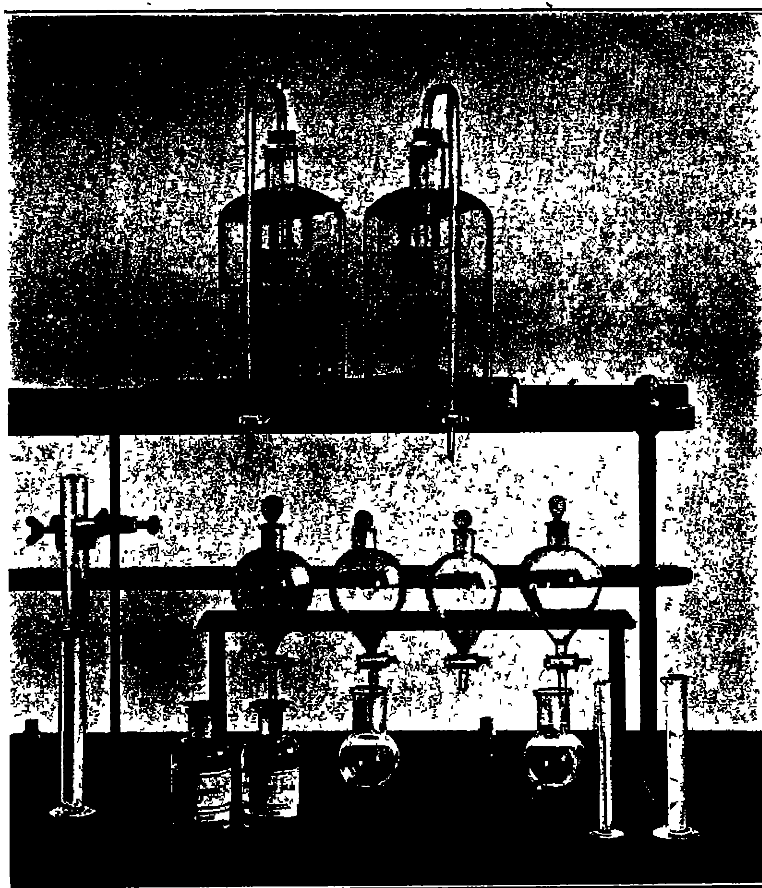


Fig. 18.—Apparatus for Alkaloid Determination.

species of *Gelidium* and closely related algæ. It occurs in long, thin, translucent pieces, nearly white, brittle when dry. The odour is slight. Agar is insoluble in cold water, but dissolves in hot water, cooling to a jelly. A solution of 1 gm. in 100 cc. of water should yield a stiff jelly on cooling. The acid-insoluble ash should not be more than 1 per cent. Some of the fragments of agar are coloured bluish-black by solution of iodine, with some areas bright red. The solution should give no precipitate with tannic acid and no blue colour with iodine.

Aloes or **aloe** is the evaporated liquid which exudes from the transversely cut leaf of various species of aloe. *Curaçao* or so-called *Barbadoes Aloes*

is the most important variety. It occurs in hard masses varying in colour from reddish-brown to nearly black. It readily fractures, the fracture being usually dull (the variety then being known as "hepatic" or "livery"), but often is transparent (known as "Capey" on account of its resemblance to the Cape variety). Its odour is characteristic.

Zanzibar Aloes is a variety of Socotrine aloes, but similar in appearance to Curaçao aloes. The odour is rather less unpleasant.

Socotrine Aloes is usually in a pasty condition, but sometimes is met with in dark brown, opaque lumps. Its odour differs from that of Curaçao aloes in being more pleasant.

Cape Aloes occurs in dark greenish-brown, vitreous masses, and has a notably sour odour.

Natal Aloes is not now a commercial article.

The active constituents of aloes have been generally considered to be barbaloin and aloe-emodin. Recently, doubt has been cast on this assumption by Kiefer,[1] who maintains that the activity is chiefly due to the resins. Since there is no quantitative method for determining the barbaloin present there is no method of analysis which gives an indication of the therapeutic value of aloes (see also Leger [2]).

Colour Tests.—The "cupraloin" reaction is given by Curaçao aloes, but by no other variety. 10 cc. of a 0·1 per cent. aqueous solution of the drug are mixed with 1 cc. of a 5 per cent. solution of copper sulphate, 1 cc. of saturated sodium chloride solution and a few drops of hydrocyanic acid. A fine deep claret colour is developed. Borntragers reaction is given by Curaçao and Cape aloes, and to a less extent by Socotrine aloes. A benzene extract of the drug is shaken with ammonia solution, when a red colour is formed. Nitric acid dropped on to a little crushed aloes gives a crimson colour with Curaçao aloes and a reddish-brown colour with Socotrine aloes.

The moisture content of aloes should not be more than 10 per cent. (B.P.), and the ash not more than 5 per cent. (B.P.). Solubility in 60 per cent. alcohol—1 gm. of the finely powdered aloes is exhausted with warm 60 per cent. alcohol, the residue being washed on to a tared filter with 60 per cent. alcohol, dried and weighed. The B.P. requires almost complete solubility.

Chloroform-Methyl Alcohol Soluble Matter.—The method proposed by Tschirch and Hoffbauer,[3] and modified by Van Itallie,[4] is of value in that it is said by the authors to separate the medicinally active constituents from the inactive resins. 5 gm. of the powdered aloes are heated in a flask with 5 cc. of methyl alcohol until homogeneous mixture is obtained. The temperature is allowed to fall to about 60° C., when 30 cc. of chloroform are added gradually, and the mixture shaken for five minutes. After standing, the clear solution is decanted and the residue heated on the water bath until the chloroform is removed. The residue is again dissolved in 5 cc. of methyl alcohol and treated as before. The process is repeated a third time and the chloroform distilled off from the combined extracts. The residue is dried at 100° C. and weighed. Owing to the scarcity of published results it is not possible to give definite limits for each variety of aloes. Van Itallie gives 78 to 88 per cent. for Curaçao, and in the authors' experience

[1] Abs., *Pharm. J.*, 1925, 115, 384.
[2] *J. Pharm. Chim.*, 118, 305.
[3] Tschirch and Hoffbauer, *Schweiz. Woch. fur Chem. und Pharm.*, 1905, 42, 12.
[4] Van Itallie, *Apoth. Ztg.*, 1906, 20, 641.

good samples have given 80 to 88 per cent. For Cape aloes, Van Itallie gives 56·2 and 82 per cent., and the authors have found 67 to 74 per cent. Socotrine aloes gives much lower figures, usually about 40 per cent. for good samples.

Althaea, or Marshmallow Root, is the dried, peeled root of *Althaea officinalis*. It occurs as yellowish-white, tapering pieces, sometimes being "limed" to improve its appearance. The drug is used for its mucilaginous properties. 1 gm. in 10 cc. of water, after standing for half an hour, should give, on filtering through cotton-wool, a pale yellow mucilage which is neutral in reaction and has no sour or ammoniacal odour. The ash should not exceed 8 per cent.

Ammoniacum is a gum-resin obtained from the stem of *Dorema Ammoniacum*, occurring in yellowish, opaque tears, brittle when cold, but soft when warm; or it may occur in darker masses. It has a faint and peculiar odour. It does not give the umbelliferone test (see Asafetida, p. 186). The chief constituents of ammoniacum are a resin consisting of an alcohol, ammoresinotannol, combined as an ester with salicylic and other acids, and gum. It also contains a trace of free salicylic acid, which gives a faint violet colour when ferric chloride is added to the solution. When the freshly broken surface is touched with a drop of a solution of sodium hypochlorite, a red colour is immediately formed. The ash should not exceed 7 per cent. and the matter insoluble in 90 per cent. alcohol should not exceed 40 per cent. (For method of determination see p. 180.)

Anise Fruit.—The fruit of *Pimpinella Anisum*. Star anise fruit, from which is distilled anise oil, is obtained from *Illicium verum*. Spanish anise fruit is the higher in price and best for pharmaceutical purposes. Anise fruit may be mixed with hemlock fruit or hyoscyamus seeds. The yield of volatile oil is from 1·5 to 3 per cent. Ash should not be more than 11 per cent. (B.P.), 9 per cent. (U.S.P.). The ash insoluble in hydrochloric acid should not exceed 1 per cent. The volatile oil should be at least 1·5 per cent.

Conium.—The following test for conium seeds is given by Brandt and Wolff[1]: the drug is distilled with aqueous potash and the acidified distillate is evaporated to dryness to remove anise oil. The residue is again distilled with potash. The presence of coniine in the distillate is shown by a brownish-white precipitate with a solution of bromine in potassium bromide solution.

Araroba or **Goa** powder occurs as an umber-brown powder. It is obtained from the trunk of *Andira Araroba*. Its chief constituent is 50 to 60 per cent. of chrysarobin, of which it should contain at least 50 per cent., as determined by exhausting 1 gm. with chloroform, distilling off the chloroform, and weighing the extracted chrysarobin. The ash varies greatly, but as long as the proportion of chrysarobin is sufficient, this is not an important matter.

Chrysarobin is a crystalline, yellow, odourless powder, obtained from araroba by extraction with hot chloroform or benzene, in which it should be entirely soluble. It contains a number of oxymethylanthraquinone derivatives. The purer forms of chrysarobin are sometimes sold as chrysophanic acid, but this is a misnomer, chrysophanic acid being a definite compound, dihydroxy-methyl anthraquinone. Chrysarobin melts between 155° and 165° C. It should be free from ash and almost entirely soluble in 90 per cent. alcohol and in hot sodium hydroxide solution. The B.P. gives

[1] *Ber. deuts. Pharm. Ges.*, 1922, **32**, 34.

the following colour tests: "About 1 mg. mixed on a white tile with a drop of fuming nitric acid produces a brownish-red liquid becoming violet on the addition of excess of solution of ammonia."

Arnica Flowers.—The flowers of *Arnica montana*. The ash content is not more than 9 per cent. (U.S.P.). Matter soluble in 45 per cent. alcohol.—The tincture (10 w/v) should contain about 2·2 w/v of solid matter.

Asafetida.—This is an oleo-gum resin obtained from the root of *Ferula fœtida*; it occurs in yellowish tears which have a strong alliaceous odour, and when broken have often a milky appearance with a pinkish tinge. It is tough and somewhat sticky at ordinary temperatures. When the freshly fractured surface is touched with nitric acid diluted with half its volume of water, a fine blue-green colour develops in a few minutes. This is not given by ammoniacum or galbanum. An alcoholic solution of asafetida, when made alkaline and considerably diluted, gives no blue fluorescence as does galbanum (due to umbelliferone), but if a tear is heated for fifteen minutes with conc. hydrochloric acid, umbelliferone is formed, and on making alkaline and diluting a blue fluorescence appears.

Ash.—Asafetida frequently contains a high percentage of mineral matter in the form of small stones, etc., but a good sample should not contain more than 15 per cent. of ash. Good specimens should not contain more than 50 per cent. of matter insoluble in alcohol (for determination see p. 180). Usual figures, 40 to 70 per cent.

Determination of Essential Oil.—50 gm. are distilled with steam until no more oil comes over. The distillate is extracted with petroleum ether, the petroleum ether distilled off, and the oil dried at a low temperature and weighed. Good specimens contain from 10 to 17 per cent. of volatile oil. The constants of the essential oil should be determined, and its sulphur content should be determined by the following method: About 0·5 gm. of the oil is weighed out into a 150 cc. flask fitted by a ground joint to a vertical condenser; 5 cc. of water are then added through the tube, followed by 5 cc. of nitric acid, and if necessary the flask is gently warmed to start the reaction, which then proceeds somewhat vigorously; 3 gm. of powdered potassium bromide are dropped in through the condenser tube, and the liquid boiled for ten minutes. On cooling, 12 cc. of 40 per cent. sodium hydroxide solution are added in the same way. The flask is disconnected and the contents washed into a platinum dish, carefully evaporated to dryness and ignited. The sulphate is then determined in the usual way. A blank determination should be made with all the materials. The sulphur found by Harrison and Self [1] varied from 17·6 to 29·2 per cent. They consider that the sulphur in the oil calculated as percentage of the drug affords a good criterion of the value of asafetida. This figure varied from 1·45 to 3·54 per cent.

Balsam of Peru is a viscid liquid, obtained from the trunk of *Myroxylon Pereiræ*. It is reddish-brown or orange-brown in colour. It has an agreeable odour and an acrid taste, producing a burning sensation in the throat. The chief constituents are benzyl cinnamate, benzyl benzoate, and cinnamyl cinnamate. Free cinnamic acid is also present. Balsam of Peru is frequently adulterated with artificial esters such as benzyl benzoate, which resemble the natural balsam in odour. S.G. 1·140 to 1·158 (B.P.). Good samples occasionally range down to 1·135.

[1] Harrison and Self, *Pharm. J.*, 1912, **34**, 205.

"*Cinnamein.*"—The B.P. requires the presence of not less than 57 per cent. of "cinnamein" when determined by the following method. Dissolve 1 gm. in 30 cc. of ether, and shake in a separating funnel with two successive quantities of 20 and 10 cc. of *N*/2 sodium hydroxide. Separate, mix the alkaline solutions, and shake with 10 cc. of ether. Draw off, and reject the alkaline solution. Add the second ethereal solution to that previously obtained. Wash with two successive quantities of 5 cc. of water. Transfer the ethereal solution to a tared flask, distil off the ether and dry at a gentle heat till the odour of ether has disappeared. Add 1 cc. of absolute alcohol, dry at 100° C. for half an hour, and weigh. The weight of the "cinnamein" obtained is not less than 0·57 gm. To the residue add 20 cc. of *N*/2 alcoholic potassium hydroxide and 20 cc. of 90 per cent. alcohol. Boil for half an hour under a reflux condenser, and titrate back with *N*/2 sulphuric acid to phenolphthalein. The saponification value obtained is not less than 235 (B.P.). Artificial balsam of Peru, made from artificial esters, usually gives a high "cinnamein" figure (about 80 per cent.), with a low saponification value.

Balsam of Tolu is obtained from the trunk of *Myroxylon Toluifera.*—It occurs as a soft, tenacious solid when fresh or in warm weather, gradually becoming more brittle on keeping. It has a fragrant odour. The chief constituents are resin esters of cinnamic and benzoic acids, free benzoic and cinnamic acids, benzyl benzoate, benzyl cinnamate, and cinnamyl cinnamate. Balsam of Tolu is almost entirely soluble in alcohol, but occasionally contains small pieces of wood or other accidental impurities. The B.P. test for balsamic acids is quite useless. The following method for the determination of free and combined balsamic acids is due to Cocking and Kettle.[1]

Free Balsamic Acids.—5 gm. of the balsam are dissolved in 25 cc. of hot alcohol in a 250 cc. CO_2 flask, 5 gm. of light magnesium oxide and 20 cc. of xylene added, and the flask shaken round until the contents are well mixed. 100 cc. of water are now added, the flask is connected to a reflux condenser, and the contents boiled for one hour. After cooling, the whole is poured on a Buchner filter, and the aqueous portion of the filtrate separated from the xylene layer, which is returned to the flask together with the filter paper and adhering magnesia-balsam magma. A second 100 cc. of water are added, and the flask again boiled for an hour, when the aqueous portion is separated as before and the extraction carried out a third time. The bulked aqueous liquids are washed once with 20 cc. of ether, then rendered acid with hydrochloric acid, and the precipitated acids extracted by shaking out with ether. The greater part of the ether is distilled off, and the residual aromatic acids dried *in vacuo* over sulphuric acid and weighed. Usual limits, 19 to 27 per cent.

Total Balsamic Acids.—2·5 gm. of the balsam are saponified by boiling with excess of *N*/2 alcoholic potash; most of the alcohol is then evaporated off, the residue dissolved in 100 cc. of hot water, and sufficient hydrochloric acid added to render the whole slightly acid. 5 gm. of light magnesium oxide and 20 cc. of xylene are next added, and the whole boiled up under the reflux condenser for one hour. The aqueous liquid is separated, the extraction twice repeated, and the bulked aqueous liquids treated as in the case of the free balsamic acids. Cocking and Kettle found a range

[1] *Y.B.P.*, 1918, 407.

of 32·68 to 47·50 per cent. for total balsamic acids in genuine balsams, and these are about the usual limits. The cinnamic acid may be estimated in the acids obtained, by the bromine method (see Benzoin, p. 189).

Acid Value.—45 to 90;[1] 112·3 to 168·5 (P.G.); 107·4 to 147·2 (B.P.).

Saponification Value.—150 to 205; 154·4 to 190·9 (P.G.); 170 to 202 (B.P.). Too much emphasis should not be laid on these limits. A lot depends on the method used. It is better to rely on the tests for balsamic acids given above.

Resin.—A petroleum ether extract obtained by warming, when treated with a dilute solution of copper acetate, should not give the characteristic green colour of the copper salts of resin acids.

Belladonna.—Both the leaves and root of *Atropa Belladonna* are used medicinally. They contain the alkaloid *l*-hyoscyamine, with a small amount of hyoscine.

Belladonna Leaves are required by the B.P. to contain not less than 0·30 per cent. of alkaloids when assayed by the following process. Into a small stoppered glass percolator, provided with a glass tap and suitably plugged with cotton-wool, introduce 10 gm. of belladonna leaves in No. 60 powder and 50 cc. of a mixture of chloroform 1 vol., and ether 4 vols. Shake, set aside for ten minutes, then add 2 cc. of 10 per cent. solution of ammonia diluted with 3 cc. of water, and set aside for one hour, shaking frequently. Then allow percolation to proceed slowly, receiving the percolate in a separator containing 6 cc. of *N* solution of sulphuric acid diluted with 20 cc. of water. When the liquid ceases to pass continue the percolation with a further 50 cc. or more of the ether-chloroform mixture, added in small quantities, until no more green colour is extracted. Shake the separator well, and after separation draw off the acid liquid into a second separator. Repeat the extraction of the ether-chloroform solution with two successive portions, each of 10 cc. of the diluted acid. Make the mixed acid solutions alkaline with ammonia, and shake out with three successive portions of 15, 15, and 5 cc. of chloroform. Evaporate the mixed chloroformic solutions to dryness, dissolve the residue in 3 cc. of ether, and again evaporate to dryness. Dissolve the residue in 10 cc. of *N*/20 solution of sulphuric acid, and titrate with *N*/20 solution of sodium hydroxide, tincture of cochineal being used as indicator. Deduct the number of cc. of the alkaline solution required from 10; multiply the difference by 0·1446; the product will be the percentage of alkaloids in the leaves. Methyl red is to be preferred as an indicator in place of cochineal. Various other processes are used for the assay of belladonna leaves. The U.S.P. method is essentially the same as the B.P., except that the ether-chloroform is in the proportion of 3 : 1, and emulsification is therefore much more likely to occur. None of the other methods is so reliable as the B.P. method,[2] though the actual time taken by the latter is longer on account of the percolation. For other methods see P.G. VI., which is unsatisfactory, and liable to give high results. Auenmuller's method[3] gives good results. Belladonna leaves contain not more than 20 per cent. of ash. The U.S.P. requires not more than 3 per cent. of acid-insoluble ash.

Belladonna Root is not standardised by the B.P. The U.S.P. requires

[1] Parry, *Parfum. moderne*, 1924, 17, 201, states that higher values are due to adulteration with colophony.
[2] Caines and Evers, *Q.J. Pharm.*, 1928, 1, 326.
[3] *Schweiz. Apoth. Ztg.*, 1920, 58, 434.

it to contain not less than 0·45 per cent. total alkaloids, and gives the following method of determination. Place 10 gm. of the drug in fine powder in a small cylindrical percolator, prepared by packing the outlet with cotton-wool. Saturate with ether-chloroform (3 : 1) by volume, add 5 cc. of dilute ammonia solution, and mix thoroughly. Macerate for one hour, pack firmly, and percolate slowly with the solvent until the drug is completely extracted, as determined by evaporating 3 or 4 cc. of the percolate to dryness, dissolving the residue in a few drops of dilute acid, and adding a drop of mercuric potassium iodide solution (Mayer's reagent), when only a very faint cloudiness should result. Transfer the liquid to a separator, rinsing the container with a small quantity of the solvent. Completely extract the alkaloid from the solvent by shaking with successive portions of dilute sulphuric acid. Extract the alkaloid with successive portions of chloroform after making alkaline with ammonia. Evaporate the chloroform from the mixed extracts, add 2 cc. of alcohol to the residue, and again evaporate. Dissolve the residue in 5 cc. of alcohol, add 5 cc. of water, and 5 cc. of $N/10$ sulphuric acid, and titrate back with $N/50$ sodium hydroxide to methyl red or cochineal. Each cc. of $N/10$ sulphuric acid used corresponds to 0·02893 gm. of belladonna alkaloids.

Benzoin.—*Sumatra Benzoin* is a solidified balsam obtained from the stem of *Styrax Benzoin*. Benzoin occurs in several varieties, of which the only one official is Sumatra benzoin, which consists of hard, brittle masses, comprised of numerous whitish tears, embedded in a dull greyish-brown resin. The odour is pleasant and similar to storax.

Siam Benzoin, obtained from a different species of *Styrax*, probably *S. Tonkinense*, occurs in tears or masses of tears, of a reddish-yellow or brown colour externally, and translucent milk-white or almond-like internally, loosely embedded in a glassy, reddish-brown resin. It has an odour more resembling vanilla than storax. Other less important varieties are *Penang Benzoin*, which resembles Sumatra benzoin, and *Palembang Benzoin*, which contains no cinnamic acid. The important constituents of benzoin are benzoic and cinnamic acids, which occur both free and combined. The B.P. 1914 states that not more than 15 per cent. should be insoluble in 90 per cent. alcohol. Siam benzoin is almost entirely soluble in 90 per cent. alcohol. The ash should not be more than 5 per cent. The chief analytical determinations in addition to that of the matter insoluble in 90 per cent. alcohol, and the ash, are the free and combined balsamic acids, which are most conveniently made by the method of Cocking and Kettle,[1] for which, see under Balsam of Tolu (p. 187). The proportion of benzoic and cinnamic acids present in the mixed aromatic acids is determined as follows. An excess of a 5 per cent. solution of bromine in carbon tetrachloride is added to the mixed acids, allowed to stand overnight, and the solvent and excess of bromine evaporated off on a water bath. The last traces of the latter are removed by several evaporations with a little ether, and the acids dried *in vacuo* over sulphuric acid and weighed. Cinnamic acid=increase in weight$\times$0·9263. Sumatra benzoin gave results up to 8·2 per cent. of free and 4·8 per cent. of combined benzoic acid, and 8·7 to 17·0 per cent. of free, and 4·6 to 16·6 per cent. of combined cinnamic acid. Siam benzoin gave about 22 per cent. of free and 12 per cent. of combined benzoic acid, with small amounts of cinnamic acid.

[1] *Y.B.P.*, 1914, 357.

Buchu Leaves are the dried leaves of *Barosma betulina*. The important constituent is the volatile oil, of which from 1·3 to 2 per cent. is present. The ash is about 4 per cent.[1]

Burgundy Pitch (*Pix Burgundica*).—This is a resinous exudation obtained from the stem of *Picea excelsa*. Burgundy Pitch is completely soluble in two volumes of glacial acetic acid, and in alcohol. Acid value, 126 to 164. Ash, negligible.

Calumba Root is the root of *Jateorhiza Columba*. Its action is due to the presence of bitter principles, which include three alkaloids—columbamine, jatrorrhizine or jateorhizine, and palmatine. Calumba should contain not more than 9 per cent. of ash, and not less than 10 per cent. of matter soluble in 60 per cent. alcohol should be present.

Canada Balsam or Turpentine (*Terebinthina Canadensis*).—A pale yellow, transparent oleo-resin, containing from 20 to 30 per cent. of volatile oil. It solidifies when mixed with 20 per cent. of its weight of moistened, heavy magnesium oxide.

Volatile Oil.—1 gm. is heated to 110° C. in a flat dish until the weight is constant. The loss represents volatile oil.

S.G. 0·985 to 0·995; refractive index, 20° C., 1·5195 to 1·5230. Acid value, 80 to 87. Oregon Balsam, which is often substituted for Canada Balsam, has an acid value of 100 to 111, and does not solidify with magnesium oxide.

Cannabis Indica, or Indian Hemp, occurs in compressed masses consisting of the flowering and fruiting tops of the plant. It contains about 15 to 20 per cent. of a soft resin, to which its physiological activity is due. The B.P. determination of matter soluble in 90 per cent. alcohol is carried out as follows. 10 gm. of the finely powdered drug and 100 cc. of 90 per cent. alcohol are shaken occasionally during twenty-four hours and filtered. 20 cc. of the filtrate are evaporated to dryness and dried at 100° C., giving not less than 0·25 gm. residue. The B.P. requires not more than 15 per cent. of ash, but this limit is often slightly exceeded by good samples. Cannabis Indica soon loses its activity by exposure to the air. It is best assayed physiologically.

Capsicum is the dried ripe fruit of *Capsicum minimum*, the pungency of which is due to the compound Capsaicin, $C_{18}H_{27}O_3N$, which melts at 64° to 65° C. Capsicum fruit should not contain more than 2 per cent. of stems, calyxes, or other foreign matter, not more than 7 per cent. of ash, and not more than 1·25 per cent. of acid-insoluble ash (U.S.P.). The non-volatile ether extract (see p. 180) should not be less than 12 per cent. (U.S.P.). The U.S.P. prescribes the following test. Mix well 1 gm. of powdered capsicum with 50 cc. of alcohol in a stoppered flask, and macerate for twenty-four hours. Dilute 0·1 cc. of the clear supernatant liquid with 140 cc. of distilled water containing 10 per cent. of sucrose; 5 cc. at this dilution swallowed at once will produce a distinct sensation of the pungency of capsicum in the throat of two out of three individuals.

Caraway Fruit (*Carui Fructus*).—The dried ripe fruit of *Carum Carvi*. The fruits contain from 3·5 to 7 per cent. of volatile oil (see p. 314), to which their action is due. The ash should not be more than 9 per cent. (B.P.); of which not more than 1·5 per cent. is acid-insoluble (U.S.P.). Ether-

[1] For methods of evaluation, see de Waal, *Pharm. Weekblad*, 1924, 61, 185, abs. *Chem. Abs.*, 1924, 1360.

soluble volatile matter (see p. 180), about 6 per cent; total ether-soluble matter, about 20 per cent.

Cardamom Seeds.—The dried ripe seeds of *Elettaria Cardamomum*. They contain from 2 to 8 per cent. of volatile oil (see p. 314). The ash should not be more than 6 per cent. (B.P.); of which not more than 5 per cent. is acid-insoluble (U.S.P.). The ether-soluble volatile matter is about 3 per cent., and the total ether-soluble matter about 6 per cent. The seeds are kept in their pericarps and separated when required for use.

Cascara Sagrada.—This is the dried bark of *Rhamnus Purshianus*, collected at least one year before being used. It contains from 1 to 4 per cent. of oxy-methyl anthraquinones, but the amount is of little value as a guide to the therapeutic value of the drug. The bark contains about 20 per cent. of *matter soluble in cold water*, and the ash should not exceed 5 per cent. The U.S.P. gives the following test. Macerate 0·1 gm. of cascara sagrada with 10 drops of alcohol, boil with 10 cc. of water, cool, filter, and shake the filtrate with 10 cc. of ether; a yellow ethereal solution separates. Shake 3 cc. of this with 3 cc. of ammonia solution; the separated ammoniacal solution, on diluting with 20 cc. of water, retains a distinct yellowish-red colour.

Oxymethyl-anthraquinones.—The following method, due to Maurin,[1] may be used for the determination of these compounds in cathartic drugs: Boil 1 gm. (in No. 45 powder) for two hours under a reflux condenser with 25 cc. of dilute sulphuric acid (1 : 4) and 100 cc. of chloroform. Cool, separate, and run off the chloroform. Shake the aqueous portion with a further 20 cc. of chloroform. Distil off the chloroform to a volume of about 10 cc. Shake the residue with 100 cc. of 5 per cent. potash solution, separate, and wash the chloroform with another 50 cc. of potash solution. Repeat until the separated alkaline liquid ceases to be coloured. Dilute the bulked alkaline extracts to 1000 cc. Compare the colour against that of a standard solution of 0·01 gm. emodin in a litre of 5 per cent. potash solution.[2]

Cascarilla Bark is the dried bark of *Croton Eluteria*. Good samples have an aromatic odour which is absent from those of poor quality. The ash should not exceed 11 per cent. and the matter soluble in 70 per cent. alcohol should be about 15 per cent.

Catechu, *Pale Catechu* or *Gambier* (Gambier, U.S.P.).—An extract of the leaves and young shoots of *Uncaria Gambier*. It occurs in cubes, having sides about 2·5 cm., brown externally and pale brown internally. Its important constituent is catechu-tannic acid. The cubes contain not more than 5 per cent. of ash (B.P.) and the powder should contain not more than 8 per cent. (B.P.). The matter soluble in 90 per cent. alcohol should not be less than 60 per cent. (U.S.P.). The B.P. figure of 80 per cent. is too high. Not less than 70 per cent. should be soluble in water (U.S.P.).

Black Catechu is an extract prepared from the wood of *Acacia Catechu*. It occurs in dark-brown, brittle masses. The B.P. ash limits are the same as for pale catechu. Not less than 60 per cent. should be soluble in 90 per cent. alcohol. It is almost entirely soluble in boiling water. When an alcoholic solution of the pale variety is made strongly alkaline with a solution of sodium hydroxide and shaken with petroleum ether, the latter shows a brilliant green fluorescence. This does not occur with black catechu. Tincture of iodine added in slight excess to an aqueous extract,

[1] *Bull. Sci. Pharm.*, abs. *Y.B.P.*, 1922, 106.
[2] See also Beal and Katti, *J. Amer. Pharm. Assoc.*, 1925, 14, 865.

gives, on boiling and cooling, a coloured and generally copious precipitate due to phlobatannins. A fresh aqueous extract, added to lime water, the latter being kept in excess, may give, after standing for five minutes, a turbidity, but should show no decided precipitation.[1]

Phlobatannins.—Dissolve 0·2 gm. of catechu in 50 cc. of water, add 10 cc. of formaldehyde solution and 10 cc. of dilute hydrochloric acid (1 : 1). Boil, filter through a Gooch crucible, wash with hot water, and dry *in vacuo*. The residue is weighed as "tannin." Hooper[2] advocates the cinchonine method for determining tannin in catechu.

Chiretta or **Chirata** is the dried plant *Swertia Chirata* collected when in flower. It is odourless, but has an extremely bitter taste. About 5 to 10 per cent. should be soluble in 60 per cent. alcohol.

Cinchona Bark.—Cinchona barks contain numerous alkaloids, the most important of which are quinine, cinchonidine, cinchonine, and quinidine. The alkaloidal content varies considerably in the different species and in the same species under different conditions of growth. The proportions of the individual alkaloids are also very variable. The total alkaloids may be as high as 12 per cent. in some cases and as low as 2 per cent. in others. Numerous species of cinchona bark have been described, the most important of which are :—

1. *Red Cinchona Bark*, from *C. succirubra*.—This is the only variety now in the B.P. It should contain from 5 to 6 per cent. of total alkaloids, of which not less than half consists of quinine and cinchonidine. It contains a large proportion of cinchonidine, which often exceeds the quinine.

2. *Yellow Cinchona Bark*, from *C. Calisaya*.—It contains about 6 per cent. total alkaloids, of which about half is quinine and cinchonidine.

3. *Pale* or *Crown Cinchona Bark*, from *C. officinalis*.—It contains about 5 per cent. of alkaloids, containing a high proportion of quinine, about 3·5 per cent.

4. *Ledger Cinchona Bark*, from *C. Ledgeriana*.—It contains 6 to 10 per cent. of total alkaloids and about 5 per cent. of quinine. It is the bark most used for the manufacture of quinine.

The U.S.P. includes all the above with the exception of *C. officinalis*. The official B.P. method for the determination of total alkaloids and of quinine and cinchonidine is as follows. Mix 10 gm. of red cinchona bark, in No. 60 powder, with 6 gm. of calcium hydroxide; add 22 cc. of water, mix intimately in a small porcelain dish or mortar, and set aside for an hour or two. Transfer this mixture to a suitable flask fitted with a reflux condenser, add 130 cc. of benzolated amylic alcohol, boil for about half an hour, and then decant the liquid on to a filter, leaving the sediment in the flask; add more of the benzolated amylic alcohol to the sediment and boil and decant as before; repeat this operation a third time, then transfer the contents of the flask to the filter, and wash by percolation with more of the benzolated amylic alcohol until the bark is exhausted. Introduce the collected filtrate, while still warm, into a stoppered glass separator, add to it 2 cc. of diluted hydrochloric acid, mix with 12 cc. of water, shake well together, and allow the liquids to separate; draw off the acid liquid, and repeat the process with water slightly acidified with hydrochloric acid, until the alkaloids have been completely removed. Carefully and exactly neutralise the acid liquid, while warm, with solution of ammonia, and concentrate by evaporation

[1] See also Ware, *Pharm. J.*, 1926, 117, 165. [2] *Analyst*, 1925, 50, 162.

to a bulk of 16 cc. To the concentrated solution add about 1·5 gm. of sodium potassium tartrate dissolved in twice its weight of water, stirring with a glass rod; after about one hour, collect the precipitate, wash, dry at 100° C. and weigh; the weight in grams multiplied by 8 gives the percentage of quinine and cinchonidine in the bark. To the mother-liquor and washings from the preceding process add solution of ammonia in slight excess and shake with three successive portions of 10 cc. of chloroform; evaporate the mixed chloroformic solutions to dryness, dry the residue at 110° C., and weigh. The weight in grams multiplied by 10 and added to the percentage of the quinine and cinchonidine gives the percentage of total alkaloids. "Benzolated amylic alcohol" consists of benzene, 3 vols., amyl alcohol, 1 vol. As pointed out by Partridge,[1] the extraction is very unsatisfactory if the above quantities are used, and it is better to use 12 cc. of water instead of 22 cc. The B.P. method even so modified is not satisfactory, and the results are low. The U.S.P. method is better and is as follows: Heat 5 gm. of cinchona in fine powder for one hour in a 500-cc. flask on a water bath with 5 cc. of dilute hydrochloric acid and 10 cc. of distilled water. Cool, add 200 cc. of ether-chloroform (3 : 1) and 10 cc. of strong ammonia, shake occasionally during two hours, allow to stand overnight, shake occasionally during half an hour and allow to settle. Decant 160 cc. of the solvent (=4 gm. cinchona) into a separator. Extract the alkaloids by repeated shaking with dilute sulphuric acid in the ordinary way. Make the acid liquid alkaline with ammonia and extract the alkaloids by repeated shaking with chloroform. Distil off the chloroform at a low temperature, dry, and weigh the alkaloids. The U.S.P. requires not less than 5 per cent. of total alkaloids. The German Pharmacopœia method is similar to the above in principle, but the determination is made by titration, which is not very satisfactory with cinchona alkaloids on account of the vagueness of the end-point. If, however, the colour change is carried to a definite hydrogen-ion concentration,[2] satisfactory results may be obtained. Bennett,[3] in a study of numerous methods, suggests Auenmuller's[4] process as the most satisfactory. This process is as follows: Heat 2 gm. of the bark in a 200 cc. bottle with 5 cc. of dilute hydrochloric acid and 17 cc. of water on a water bath for fifteen minutes. Cool, add 50 gm. of ether and 25 gm. of chloroform. Shake, add 4 gm. of 30 per cent. sodium hydroxide solution, shake continuously for ten minutes, add 2 gm. of powdered tragacanth, and shake again. Set aside for five minutes, pour off 60 gm. of the clear ethereal solution into a flask and distil to dryness. Pour three 5 cc. quantities of ether on the residue, evaporating after each addition. Dissolve in 10 cc. of warm absolute alcohol, add 3 drops of hæmatoxylin and 10 cc. of water, and titrate to a reddish-brown colour with $N/10$ hydrochloric acid. Add 30 cc. of water and titrate to lemon yellow. 1 cc. $N/10$ acid $\equiv$ 0·0304 gm. alkaloids. There are objections to the weighing of an aliquot portion of a volatile solvent, such as ether, and the titration to hæmatoxylin is far from satisfactory. The method, however, is rapid and gives good results in capable hands.[5]

[1] *Analyst*, 1919, **44**, 96.
[2] Morton, *Y.B.P.*, 1926, 447; Lizius and Evers, *Analyst*, 1922, **47**, 331.
[3] *Y.B.P.*, 1923, 678.
[4] *Y.B.P.*, 1921, 248.
[5] See also David, *C. & D.*, 1926, **104**, 438 from *Pharm. Ztg.*, 1926; Dafert and Vloek, *C. & D.*, 1926, **105**, 502 from *Pharm. Monat.*, 1926.

Cinnamon Bark.—This is the dried bark of *Cinnamomum Zeylanicum.* The essential constituent is 0·5 to 1 per cent. of volatile oil (see p. 314). The ash should not be more than 5 per cent. (B.P.) and the volatile ether-soluble matter not less than 0·5 per cent.

Cloves (*Caryophyllum*).—The dried flower-buds of *Eugenia Caryophyllata.* They contain from 15 to 20 per cent. of volatile matter (see p. 315). Ash, not more than 7 per cent. (B.P.). Acid-insoluble ash, not less than 0·75 per cent. (U.S.P.). Ether-soluble volatile matter not less than 15 per cent. (U.S.P.).

Coca leaves are obtained from species of *Erythroxylon*, viz. *E. Coca*, *E. Carthagense*, and *E. Truxillense.* Peruvian coca from the last-named variety contains a large proportion of cocaine. Java leaves contain chiefly cinnamyl cocaine, and little actual cocaine. The percentage of total alkaloids in coca leaves varies from 0·6 to 2·0 per cent. The U.S.P. VIII required not less than 0·5 per cent. of ether-soluble alkaloids. Coca leaves are not now official either in the B.P. or U.S.P. The U.S.P. VIII gave the following method of assay: Place 10 gm. of coca in No. 60 powder in an Erlenmeyer flask, add 50 cc. of a mixture of chloroform (1 vol.) and ether (4 vol.) and insert stopper securely. Allow the flask to stand ten minutes then add 2 cc. of ammonia water, and shake the flask well at frequent intervals during one hour. Transfer as much as possible of the contents of the flask to a small percolator which has been provided with a pledget of cotton packed firmly in the neck, and inserted in a separator containing 6 cc. of *N* sulphuric acid diluted with 20 cc. of distilled water. When the liquid has passed through the cotton, pack the coca firmly in the percolator with the aid of a glass rod, and, having rinsed the flask with 10 cc. of chloroform-ether mixture, transfer the remaining contents of the flask to the percolator by the aid of several small portions (5 cc.) of a chloroform-ether mixture, using the same proportions as before, and continue the percolation with successive small portions of the same liquid (in all, 50 cc.). Next shake the separator well for one minute, after securely inserting the stopper, and when the liquids have been completely separated, draw off the acid liquid into another separator. Add to the chloroform-ether mixture 10 cc. of sulphuric acid mixture, using the same proportions as before, agitate well and again draw off the acid liquid. Repeat this operation once more, drawing off the acid solution as before into the second separator, introduce a small piece of red litmus paper, add ammonia water until the liquid is distinctly alkaline, and shake out with three portions of ether (25, 20, and 15 cc.). Collect the ether solutions in a beaker, place it on a water bath filled with warm water, and allow the ether to evaporate entirely. Dissolve the residue in 3 cc. of ether, and let this also evaporate completely. To the alkaloidal residue add 4 cc. of $N/10$ sulphuric acid and 5 drops of hæmatoxylin or iodeosin solution, then titrate the excess of acid with $N/50$ potassium hydroxide solution. Divide the number of ccs. of $N/50$ potassium hydroxide used by 5, subtract this number from 4 (the 4 cc. of $N/10$ sulphuric acid taken), and multiply the remainder by 0·03, and this product by 10, to obtain the percentage of ether-soluble alkaloids contained in the Coca.[1]

Colchicum Corm and Seeds are obtained from *Colchicum autumnale.* Both the corm and the seeds are official, but no standard for alkaloids is

[1] See also de Jong, abs. *Chem. Abs.*, 1923, **17**, 2168.

given in the B.P. The active principle is the alkaloid colchicine, of which 0·4 to 0·6 per cent. is present. The ash of the corm should not be more than 6 per cent., and of the seed not more than 8 per cent.

Determination of Alkaloids.—To 10 gm. of the powder add 100 cc. of a mixture—ether, 77 cc., chloroform, 25 cc., absolute alcohol, 8 cc., and ammonia, 3 cc.—and shake during twelve hours. Filter 50 cc. through a plug of cotton-wool and distil off the solvent. Dissolve the residue in 10 cc. of ether, add 5 cc. of water and 1 gm. of paraffin wax. Distil off the ether and heat the residue until the paraffin wax forms a well-defined layer; cool, break the wax, and filter the aqueous solution into a separating funnel. Repeat the process twice, adding more ether and 5 cc. of water each time. Shake the aqueous liquid with chloroform until exhausted, distil off the chloroform, and weigh the alkaloid. The U.S.P. requires not less than 0·35 per cent. of colchicine in the corm and not less than 0·45 per cent. in the seed, as determined by the process given below. The above method, however, is less troublesome in manipulation. Place 15 gm. of colchicum seed, in fine powder, in a 500 cc. flask, and add 290 cc. of distilled water and 10 cc. of solution of lead subacetate. Weigh the flask and contents and digest the mixture at from 60° to 70° C. for three hours, with occasional agitation. Cool, add distilled water to restore the original weight, and filter off 200 cc. Add 2 gm. of sodium phosphate to the clear filtrate, or sufficient to precipitate the lead completely, shake the mixture frequently during half an hour, and filter off 100 cc., representing 5 gm. of colchicum seed. Shake out the alkaloid from the filtrate with chloroform until completely extracted, as shown by testing with iodine solution, and evaporate the chloroform solution. Add about 1 cc. of alcohol and again evaporate. Repeat this operation once more and dry the residue to constant weight at 100° C. To this weighed residue contained in a flask add 5 cc. of tenth-normal sulphuric acid and 5 cc. of distilled water, adding a few drops of chloroform, and heat the mixture for ten minutes at 70° C. Filter the liquid through a pledget of purified cotton, wash the flask and cotton with distilled water, reject the washings and filtrate, and remove as much of the water from the cotton as possible. Dissolve any insoluble residue that may remain on the cotton by washing it first with a little alcohol and then with ether; collect the alcohol-ether washings in the flask, evaporate, and dry the residue to constant weight at 100° C. Deduct this weight from the weight of residue previously obtained. The difference will be the weight of colchicine obtained from 5 gm. of colchicum seed. Davies has successfully used a method depending on precipitation with phosphotungstic acid.[1]

Colocynth Pulp (Bitter Apple).—The dried pulp of the fruit of *Citrullus Colocynthis* freed from seeds. It occurs in white, spongy, light fragments. The pulp should not contain more than 5 per cent. of seeds and not more than 2 per cent. of epicarp. It should be free from starch. The ash should be not less than 9 per cent. (B.P.) and there should not be more than 6 per cent. of acid-insoluble ash (U.S.P.).

Oil.—2 gm. extracted with petroleum ether in a continuous extraction apparatus should give not more than 2 per cent. of fixed oil. The seeds contain from 15 to 20 per cent. of fixed oil.

Conium (Hemlock).—Hemlock contains the alkaloid coniine, of which about 0·25 per cent. has been found in the leaves and 0·5 per cent. in the

[1] *Y.B.P.*, 1921, 363.

fruit. The fruit was official in the U.S.P. VIII, but conium is not now included in either the B.P. or U.S.P. When rubbed with a solution of potassium hydroxide a strong odour is produced resembling that of mice. The best method for the determination of alkaloids is that given in the U.S.P. VIII. The fruit is required to contain not less than 0·5 per cent. of coniine as determined by the following method: Macerate 10 gm. of conium in No. 60 powder for four hours by shaking with 100 cc. of a mixture of ether, 98 parts, alcohol, 8 parts, and ammonia water (10 per cent.), 3 parts. Decant 50 cc. of the clear liquid and add *N* sulphuric acid to slightly acid reaction. Evaporate off the ether by gently heating. Add 15 cc. of alcohol, and after standing in a cool place for two hours, filter off the precipitated ammonium sulphate, washing the precipitate and filter carefully with alcohol. Neutralise any excess of acid with sodium carbonate, leaving the solution faintly acid, concentrate on the water bath to 3 cc., add 3 cc. of water and 2 drops of *N* H_2SO_4, and wash with two successive portions of 15 cc. of ether to remove fat. Make slightly alkaline with sodium carbonate and shake out with successive portions of ether (15, 15, and 10 cc.). To the ethereal solution in a tared beaker add sufficient 5 per cent. hydrochloric acid to ensure excess, and evaporate off the ether by gentle heat. To the residue add 3 cc. of alcohol, evaporate, and repeat this operation to remove excess of hydrochloric acid. Dry the residue thoroughly at temperatures not exceeding 60° C. and weigh. This weight multiplied by 0·777 gives the amount of coniine in 5 gm. of drug.

Copaiba.—Copaiba is an oleo-resin obtained from various species of *Copaifera*. It contains varying proportions of oil and resin, and hence is very variable in its analytical characters. It is more satisfactory to separate the volatile oil, and to examine this and the resin separately, than to determine constants on the balsam itself. The chief commercial varieties are: Maranham, Maracaibo, Cartagena, Bahia, Para, and African. The two first are generally preferred for medicinal use, being thicker and containing only moderate amounts of essential oil. Para copaiba contains a high percentage of essential oil, and is thinner than the other varieties. African copaiba is distinguished from the other varieties by yielding a dextro-rotatory essential oil. It is sometimes used as an adulterant of the other balsams. Copaiba balsam is a more or less viscous and transparent liquid, yellow to brown in colour, occasionally showing a slight green fluorescence; the odour is pleasant and aromatic. It should be entirely soluble in absolute alcohol. The S.G. should be 0·975 to 0·995 (B.P.). This excludes the thinner balsams such as Para and Bahia, the S.G. of which may be as low as 0·920.

Volatile Oil.—About 2 gm. are accurately weighed in a flat-bottomed dish and heated at 110° C. until constant in weight, the loss being taken as volatile oil. The B.P. requires about 45 per cent. The volatile oil in the Maranham and Maracaibo varieties usually lies between 40 and 50 per cent., and should not be less than 40 per cent. In the other varieties the percentage ranges up to about 70 per cent. in the case of some specimens of Para copaiba. African copaiba is low in essential oil, usually less than 40 per cent.

Examination of the Volatile Oil.—About 50 gm. of the balsam are distilled in a current of steam superheated to 110° C. by passing through a coil heated in an oil-bath until no more volatile oil comes over. The oil

is separated, dried over anhydrous sodium sulphate, and examined as under Copaiba Oil (see p. 315).

Examination of the Résin.—The residue in the distilling flask is pressed, and dried in the oven, and the acid and ester values determined. The resin should be hard and brittle when cold. Acid value, 28 to 95 (U.S.P.). Ester value, not more than 40.

Adulterants.—The most common adulterants are African copaiba and Gurjun balsam (*q.v.*). The detection of these is described under Copaiba Oil (see p. 315). African copaiba has the following characteristics: S.G. 0·985 to 1·000; volatile oil, about 40 per cent.; acid value of resin, 110 to 120.

Coriander Fruit.—The dried ripe fruit of *Coriandrum sativum*. It is nearly globular, about 5 mm. in diameter, brownish-yellow in colour. Coriander fruit is valuable on account of its volatile oil (*q.v.* p. 315). The volatile ether extract should be not less than 0·5 per cent. Ash, not more than 7 per cent.

Cubebs are the dried, full-grown, unripe fruits of *Piper Cubeba*. The fruits are nearly globular, about 4 mm. in diameter, greyish-brown or nearly black. The odour is strong and aromatic. Crushed cubebs give a crimson colour with sulphuric acid. The ash should not exceed 8 per cent. The total ether-soluble matter should not be less than 20 per cent. (B.P.), and the volatile ether-soluble matter not less than 10 per cent. (U.S.P.). The fruits of *Piper Crassipes* and *Daphnidium Cubeba*, which are sometimes substituted for cubebs, do not give a crimson colour with sulphuric acid.

Cummin Fruit is the fruit of *Cuminum cyminum*. It consists of small oblong fruits with a peculiar odour, and taste somewhat like caraway. It contains from 3 to 4 per cent. of volatile oil, which may be determined by the methods given on p. 180.

Digitalis leaves are obtained from *Digitalis purpurea*. They owe their activity to the presence of several glucosides, viz. digitoxin (0·2 to 0·4 per cent.), which is insoluble in water, but soluble in diluted alcohol; digitalin and gitalin (0·3 to 0·9 per cent.), soluble in water, and the most valuable constituents therapeutically; also two saponins (0·6 per cent.), digitonin and gitonin. The various commercial preparations of digitalis contain varying amounts of these glucosides, according to the method of preparation, and have varying therapeutic effects in consequence (see Digitalin, p. 142). The chemical assay of digitalis is very unsatisfactory. The physiological effect of the glucosides being so different a determination of total glucosides is of little value, and, moreover, the results obtained by chemical means are not particularly satisfactory, and bear little relation to the physiological activity. Further, the determination of one constituent, such as digitoxin, gives little practical information, digitoxin not being the most desirable glucoside, and not being present at all in some of the preparations of digitalis. A physiological method of assay is therefore to be preferred, and is generally used. Digitalis seeds contain the same glucosides but in different proportions, the proportion of digitonin being greater. Digitalis leaves, if not kept in a dry atmosphere, readily lose potency. A tincture prepared in accordance with the B.P. directions should be greenish-brown in colour, and contain about 2·5 per cent. w/v of total solids.

Dill Fruit is the dried ripe fruit of *Peucedanum graveolens*. It is important on account of its volatile oil (see p. 316), of which it contains from 3 to 4 per cent. The volatile oil may be determined by one of the methods given on p. 180.

Elaterium is the dried sediment from the juice of the fruit of the *Ecballium elaterium*. It occurs in thin, flat, greyish-green pieces with a bitter and acrid taste.

Determination of Elaterin.—2 gm. are exhausted first with chloroform, then with ether, in a Soxhlet apparatus, and the extract dried and weighed. A good sample yields about 30 per cent. of elaterin ; the B.P., 1898, required a minimum of 20 per cent. Ash should not exceed 10 per cent.

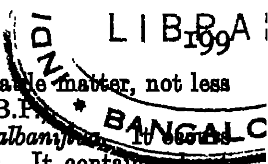
Ergot consists of the dried sclerotium of *Claviceps purpurea*, the spores of which have developed in the ovary of Rye, *Secale cereale*. The chief varieties are the Spanish and the Russian, of which the former is to be preferred for activity, and is rather larger. It is also obtained from Poland, Portugal, and Hungary. It should break with a short fracture, and be free from mould. Ergot, according to its source, contains the alkaloids ergotoxine or ergotamine, with ergotinine, the last being inactive physiologically. It also contains a number of physiologically active amines, the most important of which are histamine or ergamine (β-iminazolylethylamine), and tyrosamine or tyramine (p-hydroxy-β-phenylethylamine). There is at present no satisfactory chemical method of determining the alkaloids in ergot, since all such determinations include ergotinine, which is inactive. It is therefore standardised physiologically. Ash, 3 to 4 per cent.

Colour Test.—The following colour test [1] is given by the alkaloids, but since it is positive with ergotinine it is not a measure of the physiological activity of the drug. A sample which does not give the colour may, however, be presumed to be inactive. 2 gm. of the powdered drug are shaken during two hours with 1 cc. of 10 per cent. ammonia solution, 2 cc. of water, and 40 cc. of ether. The ether is separated, filtered, and evaporated to dryness. The residue is taken up in 15 cc. of glacial acetic acid, filtered, and 4 cc. of the filtrate are mixed with 4 cc. of 50 per cent. v/v sulphuric acid. After standing overnight a fine blue colour develops, which may be measured in a tintometer. When measured in a 1 cm. cell, 1 blue Lovibond tintometer unit is approximately equal to 0·1 mg. of alkaloid.

Eucalyptus Kino is the exudation from various species of *Eucalyptus*, but chiefly from *E. rostrata*. It occurs as dark, reddish-brown, transparent grains. It contains a large proportion of kino-tannic acid, but its composition varies according to its source. Matter soluble in water, not less than 80 per cent. (B.P.). The filtration of the insoluble matter in this determination may cause trouble. By the use of a piece of calico on the bottom of a Gooch crucible the filtration may be considerably hastened. Almost entirely soluble in 90 per cent. alcohol (B.P.). The ash is not usually more than 0·5 per cent. (the ash of Malabar Kino is over 1 per cent.). Moisture, about 15 per cent. It may be distinguished from Malabar Kino (see p. 203) by the following test.[2] If an extract is boiled with a few drops of tincture of iodine in slight excess for one minute and the mixture cooled, a precipitate is given in the case of red gum, which is soluble in solution of ammonia, whilst that given by Malabar Kino is insoluble.

Fennel Fruit is the ripe fruit of *Fœniculum vulgare*. It contains 4 to

[1] Evers, *Pharm. J.*, 1927, 118, 721. [2] Ware, *Pharm. J.*, 1926, 117, 166.



5 per cent. of volatile oil (p. 180). Ether-soluble volatile matter, not less than 4·5 per cent. Ash, not more than 11 per cent. (B.P.).

Galbanum is a gum-resin, obtained from *Ferula galbaniflua*. It occurs in rounded or irregular tears of characteristic odour. It contains about 9 per cent. of volatile oil, 60 to 66 per cent. of resin, about 20 per cent. of gum, and about 20 per cent. of umbelliferone, chiefly combined with galbaniresinotannol. The varieties are Levant and Persian. Moisture, about 10 per cent. Ash, not more than 10 per cent. Galbanum commonly contains small stones, and occasionally crystals of calcite have been found among the tears. Not more than 50 per cent. is insoluble in alcohol.

Umbelliferone Test.—If finely powdered galbanum is boiled with fuming nitric acid for fifteen minutes, cooled, diluted, and filtered, the filtrate, on making alkaline with ammonia, shows a blue fluorescence.

Galls are excrescences on the twigs of the dyer's oak, *Quercus infectoria*.

Constituents.—Gallotannic acid, 50 to 60 per cent., gallic acid, 3 per cent.

When 5 cc. of an aqueous solution of galls are boiled with 10 to 12 drops of acetic acid (33 per cent.), and 5 cc. of 0·25 per cent. solution of ferric ammonium citrate (B.P.), and the solution cooled and filtered, on adding 1 gm. of ammonium chloride and again boiling, a coloured precipitate is formed, insoluble in alcohol or aqueous ammonia.

Determination of Tannin.—1 gm. is thoroughly exhausted with hot water, and the clear filtrate treated with excess of a solution of cupric acetate. The mixture is heated to boiling, the precipitate collected on a filter paper, dried and ignited. The residue is treated with nitric acid, dried, and again ignited and weighed as CuO. Tannic acid=CuO×1·45.

Gelsemium consists of the rhizome and roots of *Gelsemium sempervirens*.

Constituents.—The alkaloids gelsemine and gelseminine, of which the drug contains from 0·15 to 0·25 per cent.

Total Alkaloids.—These may be determined by the general method (p. 181), or 10 gm. of the powdered gelsemium root may be exhausted with alcohol-ether (3 : 1), the solution evaporated, and the residue taken up with water. Lead acetate is added to this liquid, which is then filtered, and the excess of lead removed from the filtrate by hydrogen sulphide. The filtered liquid is made alkaline with sodium hydroxide, and the alkaloids extracted with ether. Since gelsemine is practically inert, it is probable that the alkaloidal content is not a measure of the activity of the drug.[1]

Gentian Root is the dried rhizome and root of *Gentiana lutea*. Gentian root has a characteristic odour and a taste, at first slightly sweet, but afterwards bitter.

Constituents.—The bitter glucosides gentiin and gentiamarin occur in the dried root, and gentiopicrin in the fresh root.

Water-soluble Matter.—5 gm. are macerated with 100 cc. of water for twenty-four hours, shaken occasionally, and filtered. 10 cc. of the filtrate yield on evaporation not less than 0·165 gm. of residue dried at 100° C. (B.P.). The U.S.P. requires not less than 30 per cent. Ash, not more than 6 per cent.

Ginger is the scraped and dried rhizome of *Zingiber officinale*. The varieties are Jamaica, Cochin, African, Japan, Bengal. Jamaica ginger has the finest aroma, Cochin being the next in quality. African ginger is more pungent and less aromatic. Jamaica, Cochin, and African gingers

[1] Pittenger, *J. Amer. Pharm. Assoc.*, 1923, **12**, 1063.

are sometimes limed to whiten them. The pungency of ginger is chiefly due to the presence of the substances gingerol, methyl gingerol, and zingerone. The moisture content should not exceed 14 per cent. Ash should not exceed 6 per cent., and the portion insoluble in water, 1·5 per cent.; insoluble in acid, not more than 0·6 per cent. Ether-soluble matter (volatile), 1 to 3 per cent. Ether-soluble matter (non-volatile), 2 to 8 per cent. (U.S.P. not less than 4 per cent.). Solubility in 90 per cent. alcohol, not less than 4 per cent., usually 5 to 7 per cent. Lower figures than the above for alcohol or ether extracts indicate exhausted ginger. Cold water extract should show not less than 12 per cent. (U.S.P.), and is usually 12 to 15 per cent.[1]

Guaiacum Wood.—The heart-wood of *Guaiacum officinale* or *Guaiacum sanctum*. It contains about 20 to 25 per cent. of resin. Ash, about 1·5 per cent. Alcohol-soluble matter, 20 to 25 per cent. The alcoholic solution assumes a blue colour on the addition of dilute ferric chloride solution.

Guaiacum Resin is the resin obtained from the stems of *Guaiacum officinale* or *G. sanctum*. It occurs as brittle, yellowish-green to reddish-brown masses or tears, breaking with a vitreous fracture. Ash, not more than 4 per cent. (B.P.). Insoluble in alcohol, not more than 10 per cent. (B.P.). The alcoholic solution is coloured blue by ferric chloride solution.

Detection of Colophony.—1 gm. of the powdered resin shaken for five minutes with 5 cc. of petroleum ether yields a colourless filtrate which does not become green when shaken with an equal volume of dilute copper acetate solution.

Guarana.—A dried paste prepared from the crushed or ground seeds of *Paullinia cupana*. It occurs in sausage-shaped cakes of a dark reddish-brown colour; very hard and somewhat glossy, with a slight chocolate-like odour. The active constituent is caffeine, 2 to 5 per cent.

Determination of Caffeine.—Weigh 6 gm. of guarana, in No. 60 powder, into a flask, add 120 cc. of chloroform and 6 cc. of ammonia solution. Shake frequently for thirty minutes and allow to stand for five hours. Again shake, and after settling filter through cotton-wool, and collect 100 cc. of the filtrate (=5 gm. of guarana). Evaporate to dryness and dissolve the residue in weak sulphuric acid at a gentle heat. After cooling, filter into a separator, and wash the flask and funnel with water. Add ammonia until alkaline, and shake out four times with 10 cc. of chloroform. Evaporate off the chloroform, dry to constant weight at 80° C., and weigh. The U.S.P. requires not less than 4 per cent. caffeine.[2]

Hamamelis Bark, or **Witch Hazel Bark,** is the dried bark of *Hamamelis Virginiana*. It contains about 6 per cent. of a tannin, hamamelitannin. Ash, about 5 per cent. An alcoholic extract when diluted with water gives the following test: Boil 5 cc. with 10 to 12 drops of acetic acid (B.P.) and 5 cc. of a 0·25 per cent. ferric ammonium citrate (B.P.) solution, cool and filter. Add 1 gm. of acid sodium phosphate and boil again; a deep brown solution or precipitate is given.

Hamamelis Leaves, or **Witch Hazel Leaves,** are the fresh or dried leaves of *Hamamelis Virginiana*. They contain tannin and a volatile oil. Ash, about 5 per cent. Tested as described under Hamamelis Bark, an extract behaves in a similar manner. 10 cc. of a dilute solution of the extract evaporated with 10 drops of dilute sulphuric acid in a porcelain dish give

[1] For analyses, see *Z. Untersuch. Nahr. Genussm.*, 1907, 14, 549–567, abs. *Analyst*, 1908, 33, 16.
[2] See also Mike, *J. Amer. Pharm. Assoc.*, 1926, 1076.

a yellow film on the side of the dish, which is not given by an extract o hamamelis bark.

Hydrastis Rhizome.—The dried rhizome and roots of *Hydrastis Canad ensis.*

Active Constituents.—Berberine, about 2·5 per cent., hydrastine, abou 1·5 per cent., and canadine. The ash should not be more than 11 per cent (B.P.); not more than 3 per cent. acid-insoluble ash (U.S.P.).

Determination of Alkaloids.—Introduce 10 gm. of hydrastis, in No. 6 powder, into a 250 cc. flask, and add 100 cc. of ether. Stopper the flask, shak it well, and allow it to stand for ten minutes, then add 5 cc. of ammonia and shake vigorously every ten minutes during two hours. Add 15 cc. o water and again shake well; when the drug has settled, decant 50 cc. of th solution (representing 5 gm. of hydrastis). Filter the solution through pledget of purified cotton into a separator, and rinse the cotton with little ether. Completely extract the alkaloids from the solution b shaking out repeatedly with weak sulphuric acid. Collect the aci washings in a separator, add ammonia solution until the solution is decidedl alkaline to litmus, and completely extract the alkaloids by shaking ou repeatedly with ether. Evaporate the ethereal solution to dryness, dr at 100° C., and weigh the alkaloids. The weight is the amount of ether soluble alkaloids from 5 gm. of hydrastis. The U.S.P. requires not less tha 2·5 per cent.

Hyoscyamus (Henbane).—The leaves of *Hyoscyamus niger.*

Active Constituent (Hyoscyamine).—The total alkaloid varies from 0·04 per cent. to 0·08 per cent. Hyoscyamus seeds contain from 0·06 to 0·1 per cent. of alkaloids. The leaves of *H. muticus* or Egyptian Henbane contai about 1·4 per cent. of hyoscyamine and the seeds from 0·87 to 1·34 per cent.

Determination of Total Alkaloids.—The B.P. gives no standard or metho of determination for alkaloids. The U.S.P. method is as follows: Intro duce 25 gm. of hyoscyamus, in No. 60 powder, into a percolator, and saturat with ether-chloroform, 3 : 1 by volume (4 : 1 by volume is preferable) After five minutes add 5 cc. of ammonia solution and mix thoroughly Percolate slowly with the solvent and proceed as under Belladonna Leave (p. 188). The U.S.P. requires not less than 0·065 per cent. total alkaloids.

Ipecacuanha.—The dried root of *Psychotria Ipecacuanha.* The officia root is chiefly obtained from Brazil; it is known also as Rio Ipecac. Th root of *Cephaelis* (*Psychotria*) *acuminata,* known as Carthagena Ipecac, i also official in the U.S.P.

Active Constituents.—The alkaloids emetine, cephaeline, psychotrine O-methyl psychotrine, and emetamine. Brazilian Ipecac contains abou 2·5 per cent. of alkaloids, of which about 70 per cent. is emetine. Carthagen Ipecac contains about 2 per cent. of alkaloids, of which less than 50 per cent is emetine. Ash, not more than 5 per cent. (B.P.).

Determination of Alkaloids, B.P.—Shake 7 gm. of the root, in No. 6 powder, frequently during five minutes, with 70 cc. of a mixture of 1 volum of chloroform and 3 volumes of ether; add 5 cc. of solution of ammoni and shake frequently during one hour; then add 5 cc. of water, or sufficien to make the powder agglomerate on violent shaking. Separate 50 cc. o the clear liquid, and shake first with 10 cc. of *N* solution of hydrochlori acid, and then with three successive portions each of 3 cc. of water. Mi the several aqueous solutions, make alkaline with solution of ammonia, an

shake out first with 10 cc. and then with three successive portions, each of 5 cc., of a mixture of 6 volumes of ether and 1 volume of chloroform. Mix the several ethereal solutions, evaporate, dry the residue at 80° C., and weigh. It should weigh not less than 0·100 gm. The B.P. standard is not less than 2 per cent. of alkaloids, the limit of error being 0·1 per cent. The U.S.P. method is similar, but ether is used as a solvent and the alkaloids are determined volumetrically. Not less than 1·75 per cent. of ether-soluble alkaloids are required. 1 cc. of *N*/10 acid corresponds to 0·024 gm. ether-soluble alkaloid. According to a report by Bliss,[1] the U.S.P. method is unsatisfactory because of the troublesome emulsions which form.

Jaborandi.—The leaves of *Pilocarpus Jaborandi* or *Pilocarpus microphyllus*. The former is now rarely seen. Jaborandi has now been dropped from the B.P. and U.S.P.

Active Constituents.—The chief alkaloids are pilocarpine, pilocarpidine, *iso*pilocarpine, and pilosine. Jaborandi contains from 0·5 to 1 per cent. of alkaloids.

Determination of Alkaloids.—The U.S.P. VIII. required a minimum alkaloidal content of 0·5 per cent. as determined by the following process: 10 gm. of the leaves, in No. 60 powder, are moistened with 2 cc. of ammonia solution and 3 cc. of chloroform, and are at once packed into a small percolator. They are percolated with chloroform containing 2 per cent. of ammonia solution until 100 cc. have been collected. The percolate is then shaken successively with 15 cc. of *N* sulphuric acid, 2 cc. of *N* sulphuric acid mixed with 8 cc. of water, and finally with 10 cc. of water. These three extracts are mixed, made alkaline with ammonia, and shaken successively with 20, 15, and 10 cc. of chloroform. The three chloroform extracts are mixed and evaporated on the water bath; the residue is dissolved in 7 cc. of *N*/10 sulphuric acid and the excess of acid is titrated with *N*/50 potassium hydroxide, using 5 drops of cochineal or odeosin solution as indicator. 5 cc. of the potassium hydroxide ≡ 1 cc. of *N*/10 sulphuric acid ≡ 0·02 gm. of alkaloids.

Jalap.—The dried tubercles of *Ipomœa Purga*.

Active Constituent, a glucoside resin, 4 to 20 per cent., usually 8 to 12 per cent.

Moisture, 12 to 16 per cent.; ash not more than 6·5 per cent. (B.P.).

Resin.—Exhaust 2 gm. of the coarsely powdered jalap with 90 per cent. alcohol in a small percolator. Distil off most of the alcohol and pour the concentrated solution obtained into eight times its volume of water. Allow to settle, filter through a weighed Gooch crucible or Soxhlet tube, wash with water, dry and weigh. The B.P. requires 9 to 11 per cent.

Jalap Resin is a mixture of resins obtained from jalap. Solubility in 90 per cent. alcohol, almost complete. Solubility in ether, not more than 15 per cent. (absence of scammony resin, B.P.). 1 gm. of the powder triturated with 20 cc. of water and filtered should give an almost colourless filtrate. A solution of 0·1 gm. in 10 cc. of sodium hydroxide solution boiled for a few minutes and cooled, when acidified with hydrochloric acid may become opalescent, but not immediately turbid (absence of certain other resins, B.P.). Moisture, 3 to 6 per cent; ash, not more than 0·5 per cent. Acid value, 10 to 15.[2]

[1] *J. Ass. Off. Agr. Chem.*, 1926, 9, 301.
[2] See also W. B. Cowie, *Pharm. J.*, 1908, 81, 363.

Jalapin (B.P.C.) is the ether-insoluble portion of Jalap resin from *Ipomœa Purga*. German jalapin is the ether-soluble resin from *Convolvulus Scammonia* (see p. 219) and *Ipomœa Orizabensis* (see below). The former is a white, odourless powder, soluble in alcohol, slightly soluble in chloroform, insoluble in ether. M.Pt. (when dry), 150° to 155° C.

Orizaba Jalap (*Ipomœa Radix*, B.P.).—Mexican scammony root. The dried root of *Ipomœa Orizabensis*. Alcohol extracts from it a resin which has the properties of scammony resin (see p. 220).

Kino.—The evaporated juice from *Pterocarpus Marsupium*. It is known as Malabar, East Indian, or Cochin kino. It occurs in small, black, glistening, angular grains free from buff-coloured cortex. The powder and the solution are red. The active constituent is kinotannic acid, 70 to 75 per cent. Should be almost entirely soluble in 90 per cent. alcohol (B.P.); not less than 45 per cent. (U.S.P.). Solubility in boiling water, not less than 75 per cent. (B.P.); not less than 80 per cent. (U.S.P.). Moisture content, about 13 per cent. Ash, not more than 2·5 per cent. (B.P.).

Tests.—A dilute aqueous extract complies with the following tests:

The precipitate, if any, given with tincture of iodine in the cold, is readily soluble in cold solution of potash (distinction from Butea gum). On boiling and cooling with tincture of iodine, however, a copious precipitate, characteristic of phlobatannins, is produced.

On boiling with formaldehyde solution and dilute hydrochloric acid (one drop of each per cc. of solution), cooling, and washing the filtered precipitate with hot water, 90 per cent. alcohol, and 5 per cent. potash solution, a coloured residue is left. A deal shaving dipped into an extract and dried, gives, on moistening with hydrochloric acid, no purple colour (distinction from kino of *Eucalyptus calophylla*).

Butea Gum, or Bengal kino, occurs in irregular, shining fragments of a very dark ruby colour. It often contains portions of cortex, but the B.P. states that it should not. It usually contains a higher percentage of ash than Malabar kino, and a lower proportion of water-soluble matter. The B.P. requires about 40 per cent. to be soluble in hot 90 per cent. alcohol. For distinction from Malabar kino, see above.

Kola.—The seeds of *Cola vera*, *C. acuminata*, and other species of *Cola*, the first variety being the most highly esteemed. The drug consists of the dried kernel of the seeds usually separated into the two cotyledons. The seeds of *C. acuminata* have four cotyledons. The active constituent is caffeine (1·5 to 3 per cent.), with traces of theobromine.

Determination of Caffeine. See Guarana, p. 200.—For preparations of kola which emulsify badly by this method, the following process should be used [1]: 2·5 gm. of kola extract or 25 gm. of fluid extract are evaporated to small bulk, dissolved in 25 cc. of simple syrup, transferred to a 250 cc. separating funnel, treated with 2·5 gm. of potassium bicarbonate, and extracted with 10 to 20 times the volume of chloroform in successive portions. The chloroform solution is filtered and evaporated to obtain the alkaloids.

Krameria (Rhatany Root).—The dried root of *Krameria triandra* (Peruvian rhatany) and also of another species of *Krameria*, probably *Krameria Argentea* (Para rhatany). The active constituent is krameria-tannic acid, 7 to 9 per cent. Ash, not more than 4 per cent. A dilute

[1] G. Meillière, *J. Pharm. Chem.*, 1912, 5, 438.

aqueous extract boiled with tincture of iodine gives a copious precipitate. That from Peruvian rhatany is insoluble in ammonia, while that from Para rhatany is soluble. The alcoholic extract is rich red in colour and gives a red precipitate with lime water. The precipitate given by copper sulphate solution and 1 drop of ammonia solution is soluble in excess of the latter (distinction from mangrove extract).

Linseed (*Linum*).—The dried ripe seeds of *Linum usitatissimum*. The chief constituents are fixed oil (30 to 40 per cent.) and mucilage. Ash, not more than 5 per cent.

Determination of Oil.—Extract 2 gm. in a continuous extraction apparatus with petroleum ether until exhausted. Not less than 30 per cent. of oil should be obtained. The oil may be examined as under Linseed Oil (p. 298). Crushed Linseed (*Lini Semina Contusa*, B.P.) should contain all the oil of the seed. Linseed contains no starch.

Liquorice Root.—*Glycyrrhizæ Radix* is derived from *Glycyrrhiza glabra* and other species of *Glycyrrhiza*. The peeled root alone is official. Varieties: Spanish or Italian (Calabrian), Russian, Persian, and Turkish.

Constituents.—Glycyrrhizin, 2 to 7 per cent., glucose, sucrose, starch, gum, etc. Ash, not more than 6 per cent. (B.P.). Not more than 2·5 per cent. should be insoluble in acid (U.S.P.).

Water-soluble Matter.—5 gm. are macerated with 50 cc. of chloroform-water for twenty-four hours, shaking occasionally, and filtered; 10 cc. of the filtrate are evaporated to dryness and should yield not less than 0·2 gm. of residue dried at 100° C. (B.P.).

Glycyrrhizin and sugars may be determined as under Liquorice Juice.

Liquorice Juice is the extract of liquorice root prepared by boiling the root with water and evaporating to a suitable consistency. It occurs in sticks (from Calabrian Juice) or blocks (Spanish Juice or Block Juice).

Constituents.—Glycyrrhizin, gum, starch, and sugars, the proportions varying widely according to the origin of the juice. Moisture should not exceed 15 per cent. Ash, not more than 8 per cent.

Starch and Gums.—5 gm. of the juice are weighed out and dissolved in 30 cc. of water on the water bath. After cooling, 50 cc. of 80 per cent. alcohol are added, the liquid being stirred during the addition. 100 cc. of 95 per cent. alcohol are then added, and after allowing to settle for half an hour the liquid is decanted through a tared filter or Gooch crucible, and the precipitate washed with 80 per cent. alcohol until the washings are colourless. The residue dried at 100° C. is weighed as starch and gummy matter.

Glycyrrhizin.—The filtrate and washings from the above are evaporated to a syrup, made up to 50 cc., and 25 cc. are transferred to a stoppered flask, graduated to hold 30 cc. Water is added up to the mark and then 3 cc. of dilute sulphuric acid (10 cc. conc. H_2SO_4 to 300 cc. water) slowly and with constant stirring. After standing all night at about 15° C. the supernatant liquid is decanted off, the precipitate washed three or four times with ice water, and finally dissolved in a little dilute alcohol with 2 or 3 drops of ammonia to neutralise traces of sulphuric acid. The liquid is evaporated to dryness in a flat-bottomed dish and weighed.

Sugars.—The remaining 25 cc. of filtrate from the starch and gums is diluted to 100 cc. and the copper-reducing power determined on 10 cc. of this solution in the usual manner (see p. 142). 50 cc. of the same solution are inverted with 2 cc. of hydrochloric acid at 70° C. for ten minutes, cooled,

neutralised, and made up to 100 cc. The copper-reducing power is determined on 20 cc. of the inverted solution. The difference between the two results is calculated to cane sugar. The following are the extremes recorded by Parry [1] for the three types of juices :—

	Italian (Calabrian).	Anatolian.	Spanish.
	Per cent.	Per cent.	Per cent.
Moisture	10·9 to 13·6	16·9 to 20·5	8·5 to 10·5
Ash	5·9 „ 7·5	5·8 „ 7·2	5·9 „ 7·1
Starch and gum . .	20·8 „ 26·0	17·5 „ 19·6	20·5 „ 23·5
Glycyrrhizin . . .	10·0 „ 12·5	18·7 „ 23·5	6·0 „ 6·6
Sugars before inversion	11·9 „ 13·5	10·9 „ 12·0	12·5 „ 14·5
Sugars after inversion .	14·5 „ 15·5	12·9 „ 13·9	14·4 „ 15·2

Lobelia.—The dried flowering herb of *Lobelia inflata*. It has a somewhat irritating odour. Active constituents : the alkaloids lobeline and lobelidine. Ash, not more than 12 per cent. (B.P.) ; not more than 5 per cent. acid-insoluble.

Ether-alcohol Soluble Matter.—Percolate 5 gm. in No. 40 powder with *Spirit Ætheris*, B.P., until exhausted. Evaporate off the solvent and weigh the extract.

Lupulin.—Glands obtained from the strobiles of *Humulus Lupulus*, the hop. A granular, brownish-yellow powder with the strong odour and bitter taste of hops. Ash, not more than 12 per cent. Ether-insoluble matter, not more than 40 per cent.

Lycopodium.—The spores of *Lycopodium clavatum*, and of other species of *Lycopodium*. A pale yellow, very mobile, odourless, tasteless powder which floats on water without being wetted. Ash, not more than 3 per cent. Lycopodium contains about 47 per cent. of fixed oil. Samples should be examined microscopically for starch and other impurities.

Male Fern.—Filix Mas. The rhizome of *Dryopteris Filix-mas*. It should not be kept for more than a year. Male Fern contains about 5 per cent. of filmarone, an amorphous acid, to which the activity is attributed. Filmarone is decomposed by hydrolysis into filicic acid and aspidinol, flavaspidic acid, albaspidin, and phloraspin, but these have no activity as tænifuges. The therapeutic value of male fern cannot be determined by chemical means, but must be determined by biological methods [2] (see *Ext. Filicis Liq.*, p. 242). The yield of liquid extract may be determined by estimating the ether extract. Ash, 2 to 3 per cent.

Manna.—A concrete saccharine exudation from the stems of *Fraxinus ornus* and *F. rotundifolia*. Yellowish-white, brittle masses with a slight, agreeable odour and sweet taste. Chief constituent, mannitol, 60 to 80 per cent. Ash, not more than 1 per cent. If 5 gm. are boiled with 100 cc. of alcohol and filtered while hot the filtrate deposits crystals of mannitol on cooling.

[1] *Foods and Drugs*, by E. J. Parry.
[2] See Wasicky, *Schweitz. Apoth. Ztg.*, 1924, 62, 601.

Mastic (Mastiche).—A concrete resinous exudation from the tree *Pistacia lentiscus.* Pale yellow, clear, glassy tears with a somewhat aromatic odour and agreeable taste. Completely soluble in ether and partially soluble in alcohol. Ash, 0·14 to 0·20 per cent. Acid value, 50 to 70. East Indian or Bombay mastic is darker in colour and more soluble in alcohol. The acid number is 103 to 109.

Mustard.—Mustard consists of the mixed seeds of white and black mustard. Black mustard seeds are the dried ripe seeds of *Brassica sinapoides*; white mustard seeds are the dried ripe seeds of *Brassica alba.*

Constituents.—Black mustard contains fixed oil (30 to 35 per cent.) and sinigrin—a glucoside which is split up into allyl isothiocyanate and dextrose by the enzyme myrosin which is also present in the seeds. White mustard contains fixed oil (20 to 25 per cent.) and the glucoside sinalbin which is split into *p*-hydroxybenzyl isothiocyanate, dextrose, and acid sinapine sulphate by myrosin. Moisture, 6 to 10 per cent. Ash, 4 to 6 per cent. Ether extract, non-volatile, 32 to 39 per cent.

Total Sulphur.—Heat 2 gm. of mustard with 10 gm. of fuming nitric acid until completely oxidised. Determine the sulphate as barium sulphate. Genuine mustard usually contains from 1·1 to 1·6 per cent. sulphur, but the figure is somewhat variable.

A *microscopic examination* should not show the presence of starch, turmeric or other adulterants.

The U.S.P. requires black mustard to yield not less than 0·6 per cent. of allyl isothiocyanate by the following process. Place 5 gm. of black mustard, in coarse powder, in a 200 cc. flask; add 100 cc. of water, stopper tightly and macerate for about two hours at about 37° C. Then add 20 cc. of alcohol and distil about 70 cc. into a 100 cc. graduated flask containing 10 cc. of 10 per cent. ammonia, and 20 cc. of *N*/10 silver nitrate solution. Mix thoroughly, stopper, allow the distillate to stand overnight; then heat on a bath of boiling water, cool, add water to make 100 cc., and filter, rejecting the first portions. Acidify 50 cc. of the filtrate, representing 2·5 gm. of black mustard, with about 5 cc. of nitric acid, and titrate with *N*/10 potassium thiocyanate, using 2 cc. of ferric ammonium sulphate T.S. as indicator. 1 cc. $N/10\ AgNO_3 \equiv 0{\cdot}004957$ gm. C_3H_5NSC.

Myrrh.—A gum-resin obtained from the stem of *Commiphora Myrrha*, and probably other species. It occurs in brittle, rounded or agglutinated tears, reddish-brown or reddish-yellow externally, more or less covered with fine powder. The odour is aromatic and the taste bitter and acrid.

Constituents.—Volatile oil, 2 to 10 per cent.; resin, 20 to 30 per cent.; gum, 50 to 60 per cent. Ash, 5 to 10 per cent. (not more than 5 per cent. of ash (B.P.); not more than 4 per cent. acid-insoluble (U.S.P.)). Not more than 70 per cent. insoluble in 90 per cent. alcohol (B.P.).

Colour Test.—The alcoholic solution evaporated so as to form a thin film yields a residue which assumes a violet colour in contact with nitric acid diluted with an equal volume of water.

Nutmeg.—The dried kernel of the seed of *Myristica fragrans.* Constituents: Fixed oil, 35 to 40 per cent.; volatile oil, 8 to 15 per cent. The U.S.P. requires not less than 25 per cent. non-volatile ether-soluble matter. See Nutmeg Oil (p. 319).

Nux Vomica.—The dried ripe seeds of *Strychnos Nux-Vomica.* Active

constituents: The alkaloids, strychnine (0·5 to 2 per cent.) and brucine (0·5 to 3 per cent.).

Total Alkaloids may be determined by the U.S.P. method as follows: Place 10 gm. of finely powdered nux vomica in a 100 cc. flask, add 100 cc. of ether-chloroform (3 : 1 by volume), stopper and shake. After standing for five minutes add 10 cc. of ammonia solution and shake for one hour in a mechanical shaker, or intermittently during two hours. Allow to stand overnight, again shake intermittently during half an hour, and then allow the drug to settle. Decant 50 cc. of the solvent and transfer to a separator, rinsing the measuring vessel with a small quantity of the solvent. Shake out with successive portions of dilute sulphuric acid, filtering each portion drawn off, until a few drops of the acid solution give not more than a very faint cloudiness with Mayer's reagent. Make the mixed acid solutions alkaline with ammonia, and extract the alkaloids with repeated quantities of chloroform until on evaporating 1 cc. of the solvent, and dissolving the residue in dilute acid, not more than a very faint cloudiness results with Mayer's reagent. Evaporate the chloroform. Dissolve the residue in neutral alcohol, add 10 cc. of $N/20$ sulphuric acid and 15 cc. of distilled water. Titrate back with $N/20$ sodium hydroxide to methyl red. 1 cc. $N/20$ $H_2SO_4 \equiv 0{\cdot}0182$ gm. alkaloid. The U.S.P. requires not less than 2·5 per cent. of total alkaloids.

Strychnine.—The B.P. requires not less than 1·25 per cent. of strychnine when tested by the following method. Shake 7·5 gm. of Nux Vomica in No. 60 powder frequently during half an hour with a mixture of 25 cc. of chloroform, 50 cc. of ether, and 5 cc. of ammonia solution. Transfer 50 cc. of the clear ethereal liquid to a separator, and extract the alkaloids by shaking with three successive portions, each of 10 cc., of N solution of sulphuric acid, transferring the acid solutions to a second separator. Make the acid solutions alkaline with solution of ammonia, and again extract the alkaloids by shaking successively with 10, 5, and 5 cc. of chloroform, drawing off the chloroform solutions into a small flask. Recover the chloroform by distillation, dissolve the residue in a mixture of 5 cc. of diluted sulphuric acid, and 10 cc. of water, heat the solution to 50° C., add 3 cc. of a mixture of equal volumes of nitric acid and water, and set aside for ten minutes. Transfer the solution to a separator, rinsing the flask with a little water, make alkaline with sodium hydroxide solution, and extract the alkaloid by shaking successively with 10, 5, and 5 cc. of chloroform. Wash the mixed chloroform solutions in a separator with 5 cc. of water, transfer to a tared dish, and allow the chloroform to evaporate, adding towards the end 5 cc. of alcohol (90 per cent.). Evaporate to dryness, dry the residue at 100° C., and weigh. This weight multiplied by 20 is the weight of strychnine in 100 gm. of the powdered Nux Vomica. Since the proportion of strychnine to total alkaloids varies only within narrow limits, the total alkaloidal content is a good indication of the value of the drug.

Olibanum (Frankincense).—A gum resin obtained from *Boswellia Carterii* and other species of *Boswellia*. It occurs in small tears, pale yellow or greenish in colour, with an agreeable odour. Constituents: Resin, 60 to 70 per cent.; gum, 27 to 35 per cent.; volatile oil, 3 to 8 per cent. Ash, not more than 10 per cent. Soluble in 90 per cent. alcohol, not less than 60 per cent. Acid value, 35 to 88.

Opium.—The juice obtained by incision from the unripe capsules of

Papaver somniferum, inspissated by spontaneous evaporation. Varieties: Turkish, Indian, and Persian Opium are chiefly used in this country. Turkish opium is used for medicinal purposes, the other varieties being used for the manufacture of alkaloids. When dry, Turkish opium contains from 12 to 15 per cent. of morphine. Persian usually gives a much lower figure than this, but is subject to great variations. The published figures for alkaloidal content are not very reliable.

Active Constituents.—Opium contains a very large number of alkaloidal constituents, of which the most important are: morphine, 7 to 15 per cent.; narcotine, 2 to 9 per cent.; codeine, 0·3 to 4 per cent.; narceine, 0·02 to 0·1 per cent.; papaverine, 0·3 per cent.; thebaine, 0·1 to 1·0 per cent. The majority of these alkaloids exist in opium in combination with meconic acid. Morphine is the most valuable constituent and the standardisation of opium is based on the morphine content.

Sampling.—This is not an easy matter, nor does there appear to be any uniform method of carrying it out. Probably the following is the most satisfactory method. Three lumps of similar size and consistency are taken out of the case, one put aside for sampling, and the other two rejected. In this way the whole case is gone through. After removing the covering leaves from a part of the surface, a cone-shaped piece is cut from each of the selected lumps, the base being about ¾-in. in diameter, and the apex as near the centre of the lump as possible. These cones are placed together in a mortar or mixer and thoroughly mixed as quickly as possible to avoid loss of moisture. The sample is then placed in an air-tight tin and portions taken for analysis.

Adulteration.—Opium may be grossly adulterated with almost any kind of heavy material, *e.g.* small shot, which are occasionally found in the lumps.

Ash, not more than 8 per cent. Moisture, 15 to 28 per cent., averaging about 23 per cent. The matter insoluble in water should not exceed 40 to 45 per cent. of the dried sample.

Requirements.—The B.P. provides that any variety of opium may be employed as a source of tincture of opium and extract of opium, provided that when dry it contains not less than 7·5 per cent. of anhydrous morphine; but, when used for official purposes other than the preparation of the alkaloids or their salts, opium must be of such a strength that when dried and powdered the resulting powder dried at 60° C. yields not less than 9·5 per cent., and not more than 10·5 per cent. of anhydrous morphine.

Determination of Morphine.—The B.P. method of determination requires: Opium in No. 50 powder, dried at 60° C., 8 gm.; calcium hydroxide, freshly prepared, 2 gm.; ammonium chloride, 2 gm.; alcohol (90 per cent.) and ether, of each a sufficient quantity; distilled water.

Triturate together the opium, calcium hydroxide, and 20 cc. of water in a mortar until a uniform mixture results; add 60 cc. of water, and stir occasionally during half an hour. To 51 cc. of the filtered liquid (representing 5 gm. of opium) in a convenient vessel add 5 cc. of alcohol (90 per cent.) and 25 cc. of ether; shake the mixture; add the ammonium chloride, shake well and frequently during half an hour; set aside for 12 hours for the morphine to separate. Counterbalance two small filters, place one within the other in a small funnel in such a way that the triple fold of the inner filter shall be superposed upon the single fold of the outer filter; wet

them with ether; remove the ethereal layer of the liquid in the vessel as completely as possible by means of a small pipette, transferring the liquid to the filter; rinse the vessel with 10 cc. of ether, again transferring the ethereal layer by means of the pipette to the filter; wash the filter with a total of 5 cc. of ether added slowly and in portions. Let the filter dry in the air, and pour upon it the contents of the vessel in portions in such a way as to transfer the granular crystalline morphine as completely as possible to the filter. When all the liquid has passed through, wash the remainder of the morphine from the vessel with morphinated water,[1] until the whole has been removed. Wash the crystals with morphinated water until the washings are free from colour; allow the filter to drain, and dry it, first at 60° C., and finally for two hours at 115° C. Weigh the crystals in the inner filter, counterbalancing by the outer filter. Dissolve 0·2 gm. of the crystals in 10 cc. of *N*/10 solution of sulphuric acid, and titrate back with *N*/10 solution of sodium hydroxide, methyl orange being used as indicator. Each cc. of the acid neutralised by the alkaloid corresponds to 0·0285 gm. of pure anhydrous morphine. The weight of pure anhydrous morphine obtained, as indicated by the titration, plus 0·051 gm., the average loss of morphine during the process, together amount to 0·5 gm., representing in 100 gm. of the dry powdered opium 10 gm. of morphine calculated as anhydrous. Limit of error, 0·5 gm. in excess or defect. The above method is designed for dry opium. When it is necessary to determine the morphine in fresh opium by the official method it is therefore necessary, in order to obtain the same conditions for precipitation of the morphine, to make some allowance for the water in the opium.[2] It is convenient for this purpose to assume an average water content of 23 per cent., and hence take 10·39 gm. as the equivalent of 8 gm. of dry opium. After mixing with the calcium hydroxide the opium is transferred by means of 77·6 cc. of water to a bottle for digestion before filtering. The 51 cc. taken represents 6·493 gm. of opium of 23 per cent. moisture content. A moisture determination is carried out at the same time, and any appreciable divergence from the average then determined can be employed to correct with sufficient accuracy the morphine result already obtained.

Instead of using counterpoised filters it is simpler to use a small weighed percolating tube containing a small plug of cotton-wool for the filtration of the morphine. This may then be attached to a pump, and gentle suction applied during the filtration and for the preliminary drying of the crystals. The digestion of the opium with the lime solution is best carried out in a rubber-stoppered bottle or flask in a warm place. Dowzard[3] digests the opium with water for an hour at 80° to 90° C., and then after adding the slaked lime shakes for two hours. This gives a better extraction of the morphine than the B.P. process. Methyl red is preferable to methyl orange as an indicator for the titration.

The U.S.P. requires that opium in its normal moist condition shall yield not less than 9·5 per cent. of anhydrous morphine. The principle of the method of determination is the same as that of the B.P., but the procedure is rather different. Introduce 8 gm. of opium, which if fresh should be in very small pieces, and if dry in fine powder, into an Erlenmeyer flask

[1] Water saturated with morphine and chloroform.
[2] Evans' *Report*, 1913, p. 46.
[3] *Pharm. J.* (iv.), 17, 909.

having a capacity of about 250 cc.; add 80 cc. of distilled water, stopper the flask, and agitate it every ten minutes (or continuously in a mechanical shaker) during three hours. Then pour the contents as evenly as possible upon a wetted filter having a diameter of not more than 12 cm., and when the liquid has drained off, wash the residue with distilled water carefully dropped upon the edges of the filter and its contents, until 120 cc. of filtrate have been obtained. Carefully transfer the moist opium to a mortar by means of a spatula and rub to a smooth paste, then rinse into the original flask with 50 cc. of distilled water, agitate thoroughly, and return the whole to the filter. When the liquid is drained off, wash the residue with 75 cc. of distilled water. Evaporate the mixed filtrates and washings on a water bath to about 40 gm. Transfer the extract to a 50 cc. graduated flask, and wash the evaporating dish with sufficient distilled water to make the entire volume measure exactly 50 cc. when cooled to room temperature. Place in a small mortar 4 gm. of freshly slaked lime, add about 10 cc. of opium extract, and rub to a smooth paste; then add the remainder of the extract, and rinse the flask with exactly 10 cc. of distilled water, adding the rinsings to the mortar, and stir frequently during fifteen minutes, avoiding unnecessary loss by evaporation. Filter through a dry filter, about 10 cm. in diameter, and transfer exactly 30 cc. of the filtrate, representing 4 gm. of opium, to an Erlenmeyer flask of suitable capacity. To this add 2 cc. of alcohol and 15 cc. of ether, and, after shaking the mixture, add 1 gm. of ammonium chloride, stopper the flask and shake it frequently during half an hour; then set it aside in a cool place for twelve hours, or overnight. Remove the stopper and brush any adhering crystals back into the flask. Decant the ethereal layer into a small funnel, the neck of which has been previously closed with a pledget of purified cotton. Rinse the flask and contents with 15 cc. of ether, and when the ether has passed through, wash the funnel and cotton with a small quantity of ether, and then pour the aqueous liquid into the funnel without trying to remove the crystals. Wash the crystals in the flask and the contents of the funnel with distilled water, previously saturated with morphine, until the washings are colourless. Then add a few drops of distilled water to replace the morphinated water. Incline the edge of the funnel over the mouth of the flask, and by means of a glass rod carefully transfer the cotton with adhering crystals to the flask. Insert the funnel into the neck of the flask and wash it with 20 cc. of $N/10$ sulphuric acid, followed by 10 cc. of distilled water, applied drop by drop round the edge of the funnel. Remove the funnel, replace the cork, warm gently, and agitate until the crystals are dissolved. Rinse the cork with distilled water, and titrate the excess of acid with $N/50$ potassium hydroxide. Each cc. of $N/10$ sulphuric acid consumed corresponds to 0·02853 gm. of anhydrous morphine. No indicator is recommended by the U.S.P. Methyl red is most suitable for the titration.

The P.G. requires that opium, when dried at 60° C., shall contain not less than 12 per cent. of morphine as determined by the following process: Rub 3·5 gm. of opium in moderately fine powder with 3·5 cc. of water, rinse into a flask with water, and bring the weight by the further addition of water up to 31·5 gm. Allow to stand with frequent shaking for one hour, and filter through a dry filter paper of 8 cm. diameter. To 21 gm. of the filtrate (=2·44 gm. opium) add 1 cc. of a mixture of 17 gm. of ammonia solution (10 per cent.) and 83 gm. of water, avoiding violent shaking, and

filter immediately through a dry 8 cm. filter paper into a flask. To 18 gm. of the filtrate (=2 gm. opium) add, while rotating the flask, 5 cc. of ethyl acetate, and a further 2·5 cc. of the mixture of 17 gm. of ammonia solution and 83 gm. of water. Close the flask and shake for ten minutes; add a further 10 cc. of ethyl acetate, and allow to stand for a quarter of an hour with occasional gentle rotation. Transfer the ethyl acetate as completely as possible to a smooth 7 cm. filter, add to the aqueous liquid remaining in the flask a further 5 cc. of ethyl acetate, rotate the mixture for a few moments, and again transfer the ethyl acetate to the filter paper. When the ethereal liquid has run through, allow the filter paper to dry in the air, pour the aqueous liquid on to the filter, disregarding the crystals sticking to the walls of the flask, and rinse the flask three times with 2·5 cc. of water saturated with ether. When the flask and the filter paper are well drained, dry both at 100° C., then dissolve the morphine crystals in 10 cc. of *N*/10 hydrochloric acid, pour the solution into a flask, wash the filter, flask and stopper with water, and dilute to about 50 cc. Add two drops of methyl red solution, and titrate with *N*/10 potassium hydroxide. 1 cc. *N*/10 HCl ≡ 0·02852 gm. morphine.

Numerous other methods for the determination of morphine have been proposed. D. B. Dott[1] suggests the following: Mix 8·8 gm. of opium with 3 gm. of slaked lime in a mortar, add 40 cc. of water, mixing by trituration for a few minutes. Transfer to a stoppered bottle, using another 40 cc. of water for the purpose. Let the bottle be occasionally shaken during one hour. Collect the mixture in a calico filter placed inside a paper filter. When fairly well drained, press the contents of the calico so as to get all the available solution into the filter paper. Mix 55 cc. of the filtrate with 3 cc. of alcohol (or methylated spirits) and 2·5 cc. of ether, adding a few drops more spirit to bring the volume after mixing to 60·5 cc. Allow to stand ten to fifteen minutes in the stoppered measure, then filter through a small filter paper to 51 cc. To this amount in a stoppered bottle add 25 cc. of ether and 2 gm. of ammonium chloride, and shake occasionally during half an hour. After eighteen hours collect the precipitated morphine in counterpoised filters in the customary manner, using water saturated with morphine and ether for the purpose of transferring the precipitate to the filter, and washing till practically free from chloride. Dry the precipitate under 100° C., wash with 12 cc. of benzene added in successive quantities of 3 cc., dry, weigh, and titrate with *N*/10 acid, using tincture of cochineal as indicator. The weight of precipitate will indicate the probable number of cc. required. Add acid till the reaction after boiling the solution is permanently acid, then cautiously add *N*/10 soda till the reaction is neutral or faintly alkaline. The number of cc. neutralised multiplied by 0·0285 indicates the amount of anhydrous morphine in the precipitate. To the number so obtained add 0·045, and multiply the sum by 20 to give the percentage of morphine in the opium. Hollman[2] shows that the best temperature for the precipitation of morphine is 16° C., and the optimum *p*H value 8·84. He states that lower temperatures retard crystallisation. The proportions of the related alkaloids seriously affect both extraction and crystallisation. The use of adsorbent charcoal introduces considerable errors. It is not possible to recommend any one simple or composite method since the variation in different opiums is too great.

[1] *Pharm. J.*, 1920, **104**, 302. [2] *Pharm. Weekblad*, 1926, **63**, 1337, 1370, 1393.

The following polarimetric method for the determination of morphine is proposed by Rakshit[1]: 16 gm. of dried opium powder are triturated with 4 gm. of slaked lime until a perfect mixture is obtained; 50 cc. of water freshly saturated with ether are added, the whole mixed, then 110 cc. of the same water are added and mixed for fifteen minutes. The solution is filtered through a covered filter into a flask. 100 cc. of the filtrate are shaken for at least three minutes in a separator with 100 cc. of ether saturated with water, and allowed to separate. The aqueous liquid, measuring about 60 cc., is shaken in another separator with an equal volume of similar ether and the process of extraction repeated a third time. 51 cc. of the separated lower liquid are placed in a 250 cc. flask with 1·5 cc. of conc. hydrochloric acid, shaken with 10 gm. of well-washed and dried animal charcoal for ten minutes, and filtered. The filtrate is examined in the polarimeter and the morphine strength calculated, taking the specific rotation of anhydrous morphine in dilute hydrochloric acid to be —127° at 25° C. with white light. The result multiplied by 1·05 gives the morphine in 5 gm. of opium.

For the colorimetric determination of morphine, see *Liq. Morphin. Hydrochlor.* (p. 253).

Determination of Narcotine and Papaverine.—The opium (1·5 gm.) is rubbed up in a mortar to a pasty condition with 4 to 5 cc. of 0·5 per cent. sulphuric acid, the acid being run in from a burette. More acid is then run in, with continual stirring, until 30 cc. in all have been added. The liquid is stirred with a pestle at intervals during half an hour, and then filtered. 20 cc. of the filtrate (=1 gm. of opium) are taken for the determination. This quantity is placed in a small beaker, heated to boiling on a water bath, and an addition of 16 gm. of sodium acetate made. The heating is continued until all the acetate has gone into solution. The beaker is well shaken and allowed to stand overnight. Its contents are filtered, and the precipitate completely transferred to the filter paper and well washed with water. The filter paper is then dried in the water oven. This renders much of the resinous and colouring matters insoluble on treatment with toluene, which is the next stage. To facilitate easy extraction with toluene, the dried precipitate is roughly powdered by rubbing one side of the paper against the other. Hot toluene is run through the filter into a separating funnel, 20 to 25 cc. in all being used. 20 cc. of 10 per cent. sodium hydroxide solution are added to the toluene and the funnel gently shaken in order to extract resinous and colouring matters from the toluene solution. The sodium hydroxide solution is then run off and the toluene shaken twice with its own volume of water, to remove sodium hydroxide. The toluene is evaporated almost to dryness in a weighed glass dish, and 2 to 3 cc. of alcohol added to facilitate crystallisation. Narcotine and papaverine rapidly separate in beautiful clusters of crystals. After drying in the oven at 100° C. these are weighed as narcotine and papaverine. The narcotine in the product is estimated by the polarimetric method, since narcotine is optically active and papaverine is inactive. A weighed quantity of the narcotine and papaverine are dissolved in a known volume of toluene and the solution is filtered and examined polarimetrically. Annett and Bose found that 2 gm. of pure narcotine, dissolved in 100 cc. toluene, gave a reading of —16·87° at 32° C. in a Hilger saccharimeter, using white light.

[1] *Analyst*, 1918, 43, 320.

Determination of Codeine.[1]—20 gm. of powdered opium and 200 cc. of water are shaken for three hours in an Erlenmeyer flask and filtered; 100 cc. of the filtrate are added to 20 cc. of strong ammonia solution contained in a similar conical flask, and the mixture shaken for an hour and then filtered. 100 cc. of this filtrate are thrice extracted with ether in a 500 cc. stoppered separator, 100 cc. being used each time. The ethereal extracts are filtered into another 500 cc. stoppered separator, and the filter paper rinsed with 20 cc. of ether. The extract and washings are twice shaken for ten minutes with a 10 per cent. w/v solution of hydrochloric acid, 25 cc. being used at a time. The two acid extracts are evaporated to dryness in a basin on the steam bath. The residue thus obtained, which is generally of a dark pink colour, is dissolved in 30 cc. of water, slightly warmed on the steam bath, the solution filtered if necessary and transferred to a separator, 50 cc. of ether and 10 cc. of a 10 per cent. solution of pure sodium hydroxide added, and the mixture shaken for ten minutes. The aqueous layer is transferred to another separator and the extraction repeated twice more with similar quantities of ether. The ethereal extracts are dried over two or three lumps of calcium chloride and filtered, the separator and the filter paper washed with 20 cc. of ether, the filtrate and washings evaporated to dryness, the residue dissolved in 10 cc. of *N*/10 sulphuric acid, and the solution titrated back with *N*/10 alkali to litmus indicator. The codeine present is calculated from the results, or, if suitable, the acid solution is filtered, made up to 50 cc. and polarised in a 200 mm. tube.

Per cent. of codeine in opium

$$=\frac{\text{Ventzke reading}\times 100\times 0{\cdot}3468\times 1{\cdot}2\times 10}{137{\cdot}5\times 2\times 2}.$$

Determination of Total Alkaloids.—The following method, due to Rakshit,[2] is suggested for the valuation of opium in this respect. Although it is admitted that the alkaloids obtained are not pure, yet it is considered valuable as a comparative method. 10 gm. of opium are triturated in a mortar with 50 cc. of water for thirty minutes or more and the liquid filtered in a Buchner funnel with the aid of a filter pump. The residue is transferred to a mortar, the filter paper being repeatedly washed into the mortar with 50 cc. of 4 per cent. hydrochloric acid, and ground well for fifteen minutes. It is again filtered. The residue is transferred to a conical flask, shaken with 200 cc. of ether, and the extract filtered at the pump; the residue is extracted twice more with 100 cc. of ether. The united ethereal extracts are repeatedly shaken in a separator with 50 cc. of the above dilute acid till the acid aqueous solution ceases to give any precipitate with an excess of sodium carbonate solution or produces merely an opalescence with Mayer's reagent. The residue from the ethereal extract and all the filter papers with adhering opium residues are rubbed well in a mortar with 25 cc. of the above dilute acid and the mixture filtered at the pump, such extractions being repeated until the extract gives only a faint opalescence with Mayer's reagent. All the aqueous and acid extracts are put together in a conical flask, treated with 2·5 gm. or more of anhydrous sodium carbonate, added only in small quantities at a time, and set aside overnight, after which the precipitate is filtered off in the same

[1] Rakshit, *Analyst*, 1921, 46, 485. [2] *Ibid.*, 1926, 51, 491.

way as the precipitate of the morphine in the B.P. process (on counterpoised double filter papers washed with water previously saturated with total alkaloids similarly obtained), dried and weighed. The alkaline filtrate, after removal of the alkaloidal precipitate, is evaporated to dryness on the water bath, finely powdered, transferred to a conical flask, and extracted repeatedly with a boiling mixture of equal volumes of chloroform and absolute alcohol (50 cc. at a time) till the extracts are practically colourless and do not give any appreciable residue on evaporation. The loss of weight is reckoned as alkaloid. The sum of these two weighings is regarded as the total alkaloids and varies from 35 to 48 per cent. in results obtained by Rakshit on Chinese, Indian, and Persian opium. Much discussion has taken place around the question of the loss of morphine from opium on keeping. Many reliable results have been published showing that no loss takes place; on the other hand there are instances that indicate that under certain conditions there has been some loss.[1]

Preparations of the mixed hydrochlorides of the total alkaloids of opium, *e.g. Opoidine, Alopon, Omnopon*, etc., are used for injection and other purposes, in order to obtain the physiological action of opium rather than that of morphine without the disadvantages of the inert matter in the drug, and a preparation known as *Opium Concentratum* is official in the P.G. These preparations are standardised to contain 50 per cent. of morphine. As it is not possible to determine all the alkaloids, analysis should be confined to the determination of the few most important ones, *e.g.* morphine, narcotine, and codeine. The preparations should be completely soluble in water, 1 in 100, and the ash should be negligible. Morphine may be determined by the official method, using 1·6 gm. instead of 8 gm. Narcotine and codeine may be determined as above. The morphine should be about 50 per cent. and the other alkaloids should of course be present in the same proportion to the morphine as they are naturally present in opium.

Opium Concentratum.—The P.G. gives the following tests. Properties: A bright brown or slightly reddish-brown powder soluble in about 15 parts of water and easily soluble in alcohol. It is insoluble in ether or chloroform. The aqueous solution is reddish brown, has a bitter taste, foams on shaking, does not change the colour of congo-red paper, and is slightly acid to litmus paper.

Narcotine and Papaverine.—Sodium acetate solution throws down a flocculent precipitate from the aqueous solution (1 in 50).

Meconic Acid.—10 cc. of the aqueous solution (1 in 50) are shaken for some minutes in a separator, after the addition of 0·2 gm. of sodium bicarbonate, with 10 cc. of a solution of 1 part of phenol in 4 parts of chloroform. After complete separation, the chloroform-phenol solution is drawn off and 10 cc. of ether are added to the aqueous liquid and the mixture well shaken. After separation, 5 cc. of the aqueous solution, after acidification with hydrochloric acid, should give no red colour with 1 drop of ferric chloride solution.

Chloride.—15 cc. of the aqueous solution (1 in 50) are treated with 1 cc. of nitric acid and 7 cc. of $N/10$ silver nitrate, warmed on the water bath until the precipitate settles, and filtered after cooling. On the addition

[1] Annett and Singh, *Pharm. J.*, 1922, **109**, 304; Sage, *ibid.*, 353; Self, *ibid.*, 373; Dott, *ibid.*, 1923, **110**, 241; *ibid.*, 1924, **112**, 337; *ibid.*, 1926, **116**, 356; Abraham and Rae, *ibid.*, **117**, 3, 32.

of a further 1 cc. of $N/10$ silver nitrate a fresh precipitate is formed. If the liquid is warmed again on the water bath until the precipitate settles, and is filtered after cooling, the further addition of $N/10$ silver nitrate causes no further turbidity. This corresponds to a content of about 8·6 to 9·7 per cent. of hydrochloric acid.

Papain.—Commercial papain consists of the dried albuminous exudate of the fruit of *Carica Papaya*. It is valuable for its proteolytic activity. It occurs as an amorphous powder, varying from white to pale brown in colour. The whiter specimens are usually more active. Starch, sugar, or pepsin have been employed to adulterate it.

Assay.—Dissolve 0·4 gm. of papain and 0·75 gm. of sodium bicarbonate in 100 cc. of distilled water. Heat to 50° to 55° C. Add 10 gm. of meat pulp prepared from lean rump steak. Digest for four hours, shaking occasionally, at 50° to 55° C. Pour into a measuring cylinder and allow to stand for half an hour. A blank without papain is carried on at the same time. Not more than 10 cc. of residue should settle out from the papain digest. Warm to 50° to 55° C., add 1·5 cc. of conc. HCl, and continue the digestion for a further four hours. Not more than 3 cc. should settle out after half an hour's standing.

The following test is also useful if meat is not available: Take two portions of 1 gm. of soluble edible casein in 20 cc. of water and add 0·05 gm. of sodium chloride. Digest at 37° C. for six hours with 0·1 gm. of papain in one tube. Acidify with 5 cc. of dilute hydrochloric acid and note the difference in the amount of precipitate obtained. In both the above tests it is preferable to carry on a digestion at the same time with papain of proved activity. The presence of pepsin is shown by the higher proteolytic activity in acid solution as compared with that in alkaline solution. Sugar, starch, etc., may be tested for in the usual manner.

Pepper (*Piper nigrum*).—Black pepper is the dried, unripe fruit of *Piper nigrum*. It contains an alkaloid (piperine), 5 to 8·25 per cent., volatile oil, 1 to 2·3 per cent., and a resin (chavicin). Ash, 2·75 to 5 per cent. Fibre, 8 to 11 per cent. Ether extract, not less than 6 per cent. Adulteration with starch will reduce all these figures.

Long pepper is the dried unripe fructification of *Piper officinarum* or of *Piper longum*. It has a similar taste and odour to black pepper, but is not so strong. It contains about 1 per cent. of volatile oil, 6 per cent. of piperine, and some chavicin. The powder is sometimes used as an adulterant of black pepper. Ash, 8·9 to 9·6 per cent. Fibre, 11·4 to 12·9 per cent. Ether extract, 4·9 to 8·6 per cent.

Physostigma.—The ripe seeds of *Physostigma venenosum* (Calabar beans). The active constituent is the alkaloid physostigmine (eserine), with small quantities of other alkaloids. The drug is not now official in the B.P. or U.S.P. The U.S.P. IX. gives the following method for determining the alkaloids and requires a minimum of not less than 0·15 per cent. Introduce 15 gm. of physostigma, in No. 60 powder, into a flask of about 250 cc. capacity, and add 150 cc. of ether. Stopper the flask, shake it well and allow it to stand ten minutes, then add 10 cc. of an aqueous solution of sodium bicarbonate (1 in 20) and shake the mixture vigorously at intervals during four hours. Now add 15 cc. of distilled water, again shake the flask well, and when the drug has settled, decant 100 cc. of the ether solution, representing 10 gm. of Physostigma. Filter the solution through a pledget

of purified cotton into a beaker and rinse the 100 cc. vessel and cotton with ether. Add 20 cc. of *N*/10 sulphuric acid and evaporate off the ether, stirring during the evaporation with a rubber-tipped glass rod. After the resinous and fatty matter have agglutinated, pour off the acid solution through a wetted filter into a separator. Redissolve the residue in the beaker in about 15 cc. of ether, add 2 cc. of *N*/10 sulphuric acid, evaporate off the ether with continued stirring as before and pour the acid solution on the filter. Repeat this operation until the whole of the alkaloid is extracted and then wash the filter with distilled water until it is free from alkaloids. Collect the solution and washings in a separator, add sufficient sodium bicarbonate to make the solution decidedly alkaline to litmus, and completely extract the alkaloid by shaking it out repeatedly with ether. Wash the combined ether solutions with 10 cc. of distilled water, separate the water completely, and filter the ether solution, washing the container and filter with ether. Evaporate the ether solution to dryness, dissolve the alkaloids from the residue in exactly 5 cc. of *N*/10 sulphuric acid, and titrate the excess of acid with *N*/50 potassium hydroxide, using cochineal as indicator. Each cc. of *N*/10 sulphuric acid consumed corresponds to 27·52 mg. of the alkaloids of Physostigma.

Pimento (Allspice).—The dried, full-grown, but unripe fruit of *Pimenta officinalis*. The chief constituent is volatile oil (see p. 320); ash, 2·5 to 5 per cent.; ether extract (volatile), 2 to 5 per cent.; fixed oil, 3·7 to 6·9 per cent.; crude fibre, 13 to 18 per cent.

Podophyllum.—The dried rhizome and roots of *Podophyllum peltatum*. It has a characteristic odour and slightly bitter taste. Indian podophyllum is from *P. Emodi.*

Determination of Resin.—The U.S.P. method is as follows: Place 10 gm. of Podophyllum in fine powder in a dry flask, add 50 cc. of alcohol, and stopper the flask with a perforated cork holding a reflux condenser. (An open glass tube of not less than 0·6 metre in length will suffice.) Place the flask on a water bath and digest for three hours with occasional shaking. Then transfer to a small percolator, allow to drain, and percolate with alcohol until the percolate measures 100 cc. Allow to cool to room temperature and add alcohol to make exactly 100 cc. Mix well. Transfer 20 cc. of this tincture, accurately measured, and representing 2 gm. of podophyllum, to a separator, add 10 cc. of chloroform and 20 cc. of a saturated solution of potassium citrate (20 gm. of potassium citrate dissolved in 12 cc. of distilled water). Shake well during two minutes, then set aside for not less than ten hours, or overnight. Draw off, discard the lower aqueous liquid, and filter the alcohol-chloroform solution through a small filter (wetted with alcohol-chloroform) into a tared flask or beaker. Rinse the separator with a mixture of 10 cc. of alcohol and 5 cc. of chloroform, and pass the rinsing through the filter. Mix the chloroformic liquids, evaporate on a water bath, dry at 100° C., and weigh. Good podophyllum contains not less than 3 per cent. of resin (U.S.P.). The above method of assay is stated by Warren [1] to give a resin which is not completely soluble in alcohol, as is required by the U.S.P. for the purity of podophyllum resin. Warren therefore prefers the method of Jenkins,[2] which is as follows:—

Place 10 gm. of the drug in No. 60 powder in a 200 cc. conical flask, and add 25 cc. of alcohol. Warm on a sand-bath at 80° C. for three hours,

[1] *J. Ass. Off. Agr. Chem.*, 1927, 10, 272. [2] *J. Ind. Eng. Chem.*, 1914, 6, 671.

after inserting a stopper fitted with a tube to act as a reflux condenser. Transfer to a small percolator and wash with alcohol until about 50 cc. of percolate are obtained. Cool and make up to 50 cc. Measure 10 cc. (=2 gm. of drug) of this tincture into a separator, and add 10 cc. of chloroform and 10 cc. of acidulated water containing 2 cc. of hydrochloric acid in 100 cc. of water. Shake, draw off the separated lower layer into another separator and extract twice more with 15 cc. of a mixture of alcohol (1 vol.) and chloroform (2 vols.). Shake the chloroform extractions with 10 cc. of acidulated water, separate, draw off the lower layer into a tared flask, and repeat the extraction of the acid liquid twice with 15 cc. of chloroform-alcohol as before. Evaporate off the solvent and dry the residue at 100° C.

Podophyllum Resin is a pale yellow to deep orange-brown amorphous powder. It should be entirely or almost entirely soluble in 90 per cent. alcohol and in ammonia solution, from which latter it is precipitated by acids. The resin obtained from *Podophyllum Emodi* (Indian podophyllum) has sometimes been substituted for the official resin. It may be distinguished by the following test :—

Add 0·5 gm. of the resin to 15 cc. of solution of ammonia diluted with 15 cc. of water. Mix thoroughly by stirring, macerate for fifteen minutes. Filter through a counterpoised filter or Gooch crucible, wash with 30 cc. of water, dry, and weigh. *Podophyllum peltatum* resin gives about 6 per cent. of residue, while *P. Emodi* resin gives about 45 per cent.[1]

Ash, not more than 1 per cent. (B.P.).

Eder and Schneiter[2] give the following method for the determination of podophyllotoxin in podophyllum resin. Shake 0·5 gm. of the finely powdered resin in a stoppered flask with 15 cc. of chloroform frequently during half an hour. Filter through a dry filter, taking care to return the first few cc. of the filtrate to the flask and covering with a watch-glass to prevent evaporation. Pour 10 cc. of the filtrate into 50 gm. (80 cc.) of petroleum ether in a tared conical flask. When the precipitate has subsided, filter through a tared Gooch crucible and wash the precipitate and flask with 20 cc. of petroleum ether. Dry the fractions of the precipitate in the Gooch crucible and in the flask for an hour at 70° C., and weigh. The total residues should correspond to not less than 40 per cent. of the weight of podophyllum resin.

Pyrethrum Root (Pellitory Root).—The dried root of *Anacyclus Pyrethrum*. Chief constituent, an alkaloid pyrethrine. Ash, not more than 5 per cent. (U.S.P.). Solubility in 70 per cent. alcohol, about 12 per cent.

Pyrethrum Flowers (Insect Flowers).—The dried, unexpanded flower heads of *Chrysanthemum Cinerariæfolium* and *C. Coccineum*, the former yielding the Dalmatian and the latter the Persian or Caucasian drug. The unexpanded flowers are more active; they lose their activity as they expand. Active constituents, pyrethrin. Moisture, about 10 per cent. Ash, 8 to 9 per cent. Ether extract, non-volatile, which contains the active principle, should amount to 7·5 to 10·5 per cent., and should be of a golden yellow colour, not green (absence of an excess of stem).

Quassia.—The wood of the trunk and branches of *Picræna excelsa*, or *Picrasma excelsa* (Jamaica Quassia), or of *Quassia amara* (Surinam quassia). The wood is odourless, but has a very bitter taste. Active constituents:

[1] Dott, *Pharm. J.*, 1923, 111, 661.
[2] *Pharm. Acta. Helv.*, 1926, 1, 18.

Jamaica quassia contains the two crystalline bitter principles α- and β-picrasmin, a mixture of which is known as quassiin, and melts at 210° to 211° C. Commercial quassin or quassine is a variable product, which must be distinguished from the active principle. Ash, about 4 per cent. Solubility in 45 per cent. alcohol, not less than 5 per cent. (usual figures 5·2 to 7·3 per cent.).

Quillaia (Soap Bark).—The dried inner part of the bark of *Quillaja saponaria*. When shaken with water the powdered bark forms a copious, persistent froth.

Constituents.—The two saponins—quillaic acid and quillaic sapotoxin. Ash, not more than 15 per cent. (B.P.). Solubility in 60 per cent. alcohol, about 25 per cent.

Saponin.[1]—Extract 20 gm. of the finely cut bark with four successive quantities of about 100 cc. of boiling water. Boil the filtrates (clarified if necessary with fuller's earth) with 50 cc. of conc. hydrochloric acid for an hour. Cool, and filter off the sapogenin through a tared filter paper, wash, dry to constant weight at 100° C., and weigh. One part of sapogenin =3·22 parts of saponin. About 10 per cent. of saponin should be obtained.

Saponin.—Commercial saponin is an amorphous, white or yellowish-brown powder, soluble in water or hot alcohol. A dilute aqueous solution froths strongly on shaking. When 2 gm. are treated by the above method for quillaia the percentage of saponin found should be not less than 60 per cent. The ash is about 9 per cent.

Rhubarb (Rheum).—The rhizome of *Rheum palmatum* or *R. officinale* and other species of *Rheum* collected in China and Tibet, or of *Rheum Rhaponticum* or *R. officinale*, grown in Europe. The varieties are Shensi and Canton, the former being the most valuable.

Constituents.—Rhubarb contains a number of anthraquinone derivatives in the free state and in combination, viz. rhein, emodin, aloe-emodin, emodin monomethyl ether, chrysophanic acid, and a compound $C_{14}H_{12}O_3$, probably trihydroxy-dihydroanthracene. The total anthraquinone derivatives vary from 3 to 4·5 per cent., but the amount probably has little relation to the value of the drug.[2] *Rheum Rhaponticum* contains the anthraglucoside rhaponticin, but no aloe-emodin, emodin, or rhein. To these anthraquinone derivatives the purgative properties of rhubarb are due. The astringent action is chiefly due to free gallic acid. Ash, not more than 15 per cent. (B.P.). Solubility in 45 per cent. alcohol, not less than 30 per cent.

Tests.—On the addition of alkali to powdered rhubarb a red colour is formed. The U.S.P. gives the following test for identity: Boil 1 gm. of powdered rhubarb with 10 cc. of an aqueous solution of potassium hydroxide (1 in 100); allow it to cool, filter, acidulate the filtrate with hydrochloric acid, and shake with 10 cc. of ether; the ethereal layer is coloured yellow on standing. Shake this ethereal solution with 5 cc. of ammonia solution; the latter is coloured cherry red (presence of emodin), and the ethereal solution remains yellow (presence of chrysophanic acid).

The presence of *Rheum Rhaponticum* may be detected by the following test: Shake 0·5 gm. of the powdered drug with normal ammonia solution for fifteen minutes at a temperature of 25° to 30° C. Filter on to a watch-glass and allow to crystallise. Pure rhapontic rhubarb, or mixtures

[1] Cofman-Nicoresti and Tallantyre, *Y.B.P.*, 1920, 446.
[2] For method of determination, see p. 191.

containing a large proportion of it, deposit abundant crystals of rhaponticin of characteristic microscopic appearance.

Santonica.—This drug is only of importance as the source of Santonin (see p. 171). It consists of the dried, unexpanded flower-heads of *Artemisia maritima* var. *Stechmanniana*, which is the chief source of the santonin of commerce. Other species of *Artemisia* contain santonin, *e.g.* the leaves of *A. brevifolia* have been found to contain about 1 per cent.[1]

Determination of Santonin.[2]—13 gm. of the drug in medium fine powder are placed in a separator, the stem of which is plugged with cotton, and shaken occasionally for one hour with 130 gm. of chloroform. Then 102·5 gm. of the solution (=10 gm. of drug) are run off into a 200 cc. tared Erlenmeyer flask. The chloroform is distilled off until the residue weighs between 7 and 8 gm. To this, 100 gm. of saturated barium hydroxide solution are added, and the flask placed in the hot water-bath until all the chloroform is driven off. The liquid is filtered, the filter washed with a little boiling water, and the filtrate acidified with 5 gm. of 25 per cent. hydrochloric acid, heated on the water bath for a few minutes, and then, when lukewarm, transferred to a separator. The flask is rinsed out with 20 cc. of chloroform, and the latter added to the separator. The contents of the latter are then shaken briskly for two minutes. The chloroform is drawn off into a 100 cc. Erlenmeyer flask, and the aqueous liquid extracted twice more with 20 cc. each of chloroform. The chloroform is evaporated, the residue taken up by warming with exactly 7·5 gm. of absolute alcohol, and then mixed with 42·5 gm. of hot water. The milky solution is filtered immediately into a tared 100 cc. flask, and the filter and flask rinsed with two portions of 10 cc. each of a mixture of 3 gm. absolute alcohol and 17 gm. of water. The liquid is then allowed to stand for twenty-four hours. The separated santonin is collected on a tared filter, the flask and filter washed with two portions of 10 cc. each of the above diluted alcohol, and flask and filter dried to constant weight. To the weight of santonin found, 0·04 gm. should be added to allow for that remaining dissolved.[3]

Van Itallie[4] gives the following test for santonin in Artemisia. The test is carried out in a glass ring about 1·5 cm. in diameter and 2 to 3 mm. in height, placed on a slide. 50 mgm. of wormseed are placed within the ring, and the slide is heated on a small metal disc by means of a micro-burner. After a few minutes, when the moisture has been driven off, the ring is covered by a slide and the heating continued until a convenient sublimate is obtained on the slide. If crystals of santonin are not evident under the microscope, the sublimate is moistened with a drop of alcohol and rubbed with a platinum wire. If santonin is present, crystals will be formed which are remarkable for their strong polarising properties, and may be identified by the melting-point or by the red colour formed with hot alcoholic potash.

Scammony Root.—The dried root of *Convolvulus Scammonia*. Active constituent, scammony resin, of which it contains from 3 to 13 per cent. (average about 8 per cent.). Ash, about 10 per cent.

[1] Greenish and Pearson, *Pharm. J.*, 1921, **106**, 2; Greenish and Maplethorpe, *Y.B.P.* 1923, 646.

[2] Engelhardt and O'Brian, *Drugg. Circ.*, 1913, **57**, 443, abs. *Y.B.P.*, 1914, 138.

[3] See also Eder and Schneiter, *Schweitz. Apoth. Zeit*, 1925, **63**, 405.

[4] *Pharm. J.*, 1923, **57**, 632.

haust 5 gm. of the coarsely powdered root with 90 per cent. l off most of the alcohol, pour the concentrated solution s its volume of water; allow the resin to settle, wash with weigh.

Resin.—A mixture of resins obtained from scammony root a jalap root (Mexican scammony). Scammony resin should soluble in alcohol. On shaking 1 gm. with 20 cc. of water and ltrate is almost colourless (B.P.). The B.P. requires that 75 per cent. shall be soluble in ether. This test has been f no value as a test of purity and quality, and the results been shown to vary with the amount of solvent used and he ether.[1]

akeroot).—Senega root is the dried root of *Polygala senega.* r of methyl salicylate.

stituents.—Two saponins, viz. an acid glucoside, polygalic utral glucoside, senegin. Ash, about 4 per cent. Solubility alcohol, about 30 per cent.

nna leaves are the dried leaflets of *Cassia acutifolia* and of *folia*, senna pods being the corresponding dried ripe fruits. xandrian and Tinnevelly or Indian senna are the most eties.

stituents.—Rhein and aloe-emodin. Ash, of leaves, not more it.; not more than 3 per cent. acid-insoluble (U.S.P.).

a gives the emodin test as follows: Mix 0·5 gm. of powdered cc. of an alcoholic solution of potassium hydroxide (1 in 10), two minutes, dilute with 10 cc. of water, and filter. Acidify h hydrochloric acid, shake it with ether, remove the ethereal e it with 5 cc. of ammonia. A red colour is formed.

—Serpentary rhizome is the dried rhizome and roots of *rpentaria* (Virginian serpentary), and of *Aristolochia reticu-* pentary). Active constituents: volatile oil (1 to 2 per cent.), yellow, crystalline bitter). Ash, 6 to 10 per cent. Solubility alcohol, about 20 per cent.

a).—Squill is the bulb of *Urginea Scilla*, divested of its dry uter scales, cut into slices, and dried. The white variety *itima* is official in the U.S.P. The activity is due to a gluco- ides, several of which have been described—*e.g.* scillitin, nd scillaren, but nothing is known of the chemistry of these. $_{25}O_6$, melts at 152° to 154° C.[2] Ash, not more than 5 per ty in 60 per cent. alcohol, 65 to 80 per cent. Squill is assayed by a biological method.

Seeds (Staphisagria Seeds).—Stavesacre seeds are the dried *elphinium Staphisagria.*

s.—Fixed oil, about 30 per cent.; alkaloids, about 1 per g of delphinine, delphisine, delphinoidine, and staphisa- 10 to 15 per cent. Ether extract, non-volatile, about 30 aloids, estimated by general method (see p. 181), 1·0 to 1·5

Edmonton, *Y.B.P.*, 1921, 316; see also Bourdier, *J. Pharm. Chim.*, 1912,

i, *Compt. rend.*, 1914, 158, 1520.

Storax (*Styrax Præparatus*, B.P.).—Prepared storax is a viscid balsam obtained from the wounded trunk of *Liquidambar orientalis*, and purified by solution in ethyl alcohol, filtration, and evaporation of the solvent. Crude storax is an opaque, greyish, viscid liquid, containing from 20 to 30 per cent. of water, fragments of bark, etc. The purified balsam forms a brownish-yellow, viscid mass, entirely soluble in alcohol or ether.

Constituents.—Resin (storesinol) partly combined with cinnamic acid, vanillin, styrol, cinnamyl cinnamate (styracin), ethyl cinnamate, phenylpropyl cinnamate, and free cinnamic acid. The B.P. states that storax shall lose not more than 5 per cent. of its weight when heated in a thin layer on a water bath for one hour. Acid value, 60 to 90. Ester value, 100 to 146.

The B.P. requires that storax shall yield not less than 20 per cent. by weight of cinnamic acid when tested by the following process: Dissolve 2·5 gm. of the storax in 25 cc. of *N*/2 alcoholic solution of potassium hydroxide, boil for one hour under a reflux condenser, neutralise with *N*/2 solution of sulphuric acid, remove the alcohol by evaporation, and dissolve the residue in 50 cc. of water. Shake this aqueous solution with 20 cc. of ether; after separation remove the ethereal layer, wash it with 5 cc. of water, and add the washings to the aqueous solution, rejecting the ethereal liquid. Acidify the aqueous solution with diluted sulphuric acid, and shake it with four successive portions, each of 20 cc. of ether. Mix the ethereal solutions, wash with a few cc. of water, transfer to a flask, and distil off the ether. To the residue add 100 cc. of water and boil vigorously for fifteen minutes under a reflux condenser. Filter the solution while hot, cool to 15·5° C., and collect on a tared filter the crystals of cinnamic acid that have separated. Repeat the extraction of the residue with the filtrate at least three times, or until no more cinnamic acid is removed. Press the filter paper and crystals between blotting paper, dry in a desiccator over sulphuric acid, and weigh. Add to the weight of the crystals so ascertained 0·03 gm. (representing the average amount of cinnamic acid remaining dissolved in the aqueous liquid). The total weight is not less than 0·5 gm. The above method is long and tedious, but is the most satisfactory of those suggested. Very few samples of storax of good quality are now obtainable.

Stramonium.—Stramonium leaves are the dried leaves of *Datura Stramonium*. The U.S.P. requires not more than 3 per cent. of stems over 8 mm. in diameter. Ash, not more than 18 per cent. The U.S.P. requires not more than 4 per cent. of acid-insoluble ash.

Stramonium seeds contain from 0·2 to 0·5 per cent. of the alkaloids, hyoscyamine and hyoscine, but no atropine. About 25 per cent. of fixed oil is also present.

Assay.—Place 10 gm. in fine powder in a separator plugged with cotton, cover with ether-chloroform (4 vols. ether, 1 vol. chloroform), and allow to stand for five minutes. Add 5 cc. of ammonia and mix thoroughly. After macerating for an hour percolate slowly with the solvent until exhausted, collecting the percolate in another separator. The percolation must be continued until on evaporating 3 or 4 cc. of the percolate, dissolving the residue in a few drops of dilute acid, and adding a drop of Mayer's reagent only a very faint cloudiness results. Extract the alkaloid from the solvent by shaking with successive portions of dilute sulphuric acid,

filtering each portion of the acid liquid through a plug of cotton-wool, until a few drops give not more than a faint opalescence with Mayer's reagent. The acid liquid is then made alkaline with ammonia, and extracted with successive portions of chloroform until the alkaloid is extracted, the test for alkaloid being carried out as before. The chloroform is then evaporated off, 1 cc. of neutral alcohol added, and evaporated. The residue is dissolved in 3 cc. of neutral alcohol and 10 cc. of $N/20$ hydrochloric acid added. The excess of acid is titrated back with $N/20$ sodium hydroxide to methyl red. 1 cc. $N/20$ HCl ≡ 0·01446 gm. hyoscyamine.

Strophanthus Seeds.—The dried ripe seeds of *Strophanthus Kombé* freed from the awns. *S. hispidus* is also official in the U.S.P. Several varieties of strophanthus seeds are to be found in commerce. The botanical features of these varieties are so closely allied that commercial samples are usually admixtures. In addition to the two varieties mentioned above, the following may be met with, *S. Courmontii*, *S. Nicholsoni*, *S. gratus*, *S. emini*, and *S. Preussii.*[1]

Sulphuric Acid Test.—When the seeds are sliced longitudinally and the exposed cotyledons moistened with a drop of 80 per cent. by volume sulphuric acid, a fine green colour is developed in a few minutes with *S. Kombé*, *S. hispidus, and S. Preussii.* A red colour is given by *S. Courmontii. S. Nicholsoni*, *S. gratus*, and *S. emini*. In examining commercial samples, at least 20 seeds should be tested in this way in order to determine the percentage which respond to the test. Bohrisch[2] recommends the following procedure as being most reliable. Thin cross-sections of the seeds are placed on a watch-glass and treated with a little ether to remove fat. They are then covered with a drop of sulphuric acid which has been diluted with one-fourth of its volume of water.

Determination of Strophanthin.—The best method is that of Cæsar and Loretz.[3] 7 gm. of the finely crushed seeds are boiled in a reflux apparatus for an hour with 70 gm. of absolute alcohol. When cold the whole is made up to the original weight with absolute alcohol and 50·5 gm. are filtered into a porcelain basin. The alcohol is evaporated and the residue washed with petroleum ether, which is poured through a filter. The insoluble residue in the filter and basin is boiled with 5 to 8 gm. of water, treated with 5 drops of lead acetate solution and 0·2 gm. of kieselguhr, well mixed, and filtered into a 100 cc. flask. The insoluble portion is washed until the runnings no longer have a bitter taste. The filtrate is treated with 5 drops of hydrochloric acid and boiled gently for two hours, the volume being kept between 10 and 20 cc. by the addition of distilled water. When cold the liquid is extracted twice with 10 cc. of chloroform, which is filtered into a tared flask. The aqueous portion is again boiled for half an hour and extracted three times with 10 cc. of chloroform. If the aqueous solution still tastes bitter, the boiling and extraction with chloroform are repeated. The chloroform is distilled off and the residue dried and weighed. It consists of strophanthidin, one part of which corresponds to 2·187 parts of pure strophanthin. According to K. Samaan,[4] methyl alcohol is the best solvent next to water for extracting the active principle, and probably it would be an advantage to use it in the above process.

Tar (Stockholm Tar), *Pix Liquida.*—Stockholm tar is obtained by the

[1] K. Samaan, *Pharm. J.*, 1922, **109**, 83.
[2] *Pharm. Zeit.*, 1918, **63**, 318.
[3] *Ibid.*
[4] *Y.B.P.*, 1919, **345**.

distillation of the wood of *Pinus sylvestris* and other species of *t*
S.G., 1·02 to 1·15. On shaking with water and filtering, the aqueous solution is acid, and is coloured reddish by dilute ferric chloride solution. Stockholm tar is completely soluble in ten times its own volume of 90 per cent. alcohol.

Coal Tar (*Pix Carbonis Præparata*, B.P.).—Coal tar is almost entirely soluble in benzene or chloroform, and only partially soluble in 90 per cent. alcohol or ether. On shaking with water and filtering, the filtrate is alkaline.

Valerian.—The dried rhizome and roots of *Valeriana officinalis*. Chief constituent, volatile oil (0·5 to 1 per cent.); ash, not more than 10 per cent. (B.P.).

Vanilla.—The prepared unripe fruit of *Vanilla planifolia* (Andrews). Chief constituent: Vanillin (methyl-protocatechuic aldehyde, $C_6H_3OCH_3OH.CHO$), 1·5 to 2·9 per cent. The best variety of vanilla is the Mexican, other varieties being Java, Bourbon, Ceylon, Tahiti, etc.

Determination of Vanillin (Busse's method).—20 gm. of the pods crushed with sand are exhausted with ether in a Soxhlet tube, and the ethereal extract shaken out with 20 per cent. sodium bisulphite solution. From the latter, vanillin is removed by treatment with dilute sulphuric acid, the sulphur dioxide formed being removed by a current of carbon dioxide. The vanillin is extracted by shaking out with ether, evaporating the solvent, and weighing the residue.

Venetian Turpentine.—This is the crude turpentine obtained by boring into the heartwood of the larch, *Pinus larix* (Linn.). Venice turpentine contains about 20 per cent. of essential oil, the remainder being resin. A mixture of ordinary turpentine oil and resin is frequently sold as Venice turpentine. Larch turpentine is completely soluble in alcohol, ether, or chloroform. Acid value, 64 to 77; ester value, 35 to 56; saponification value, 108 to 133.

Hirschsohn's Test.—1 cc. of the turpentine is treated with 5 cc. of dilute ammonia solution (S.G. 0·96). Larch turpentine remains clear, whilst ordinary turpentine forms a milky emulsion. When the lower layer of the larch turpentine is stirred it gradually becomes semi-solid and opaque. In the case of ordinary turpentine the lower layer mixed with the ammonia forms a milky emulsion which rapidly solidifies to a gelatinous mass.

Volatile Oil.—A weighed quantity of about 2 gm. is heated in a flat dish on the water bath until constant in weight. Not less than 15 per cent. should be lost.

SECTION II.

DRUGS OF ANIMAL ORIGIN.

Cantharides (Spanish Flies).—The dried beetles *Cantharis vesicatoria*. *Mylabris* or *Chinese Cantharides* are the dried insects *Mylabris phalerata* or *Mylabris Cichorii*. Both are vesicants, and both owe this property to the presence of Cantharidin (see p. 136). Cantharides contain from 0·4 to 1 per cent., and Mylabris 1 per cent. or more of cantharidin. The U.S.P. requires not less than 0·6 per cent. Cantharides are no longer official in the B.P. They have been replaced by cantharidin, which may be prepared from various species of *Cantharis* or *Mylabris*. Cantharides with an ammoniacal odour should not be used. The moisture content should be not more than 10 per cent. (U.S.P.).

Determination.—The U.S.P. method for the determination of cantharidin is as follows: Place 15 gm. of cantharides in moderately coarse powder in a stout bottle of not less than 250 cc. capacity, add 150 cc. of a mixture of benzene, two volumes, and purified petroleum benzine one volume, and then add 2 cc. of hydrochloric acid. Stopper the bottle tightly, shake it well, and allow it to stand about ten hours. Now gradually warm the bottle and its contents to about 40° C., and maintain it at approximately that temperature with frequent shaking during three hours, avoiding evaporation. If necessary add additional solvent to replace any lost by evaporation. Cool the mixture, decant or filter off 100 cc. of the clear solution, and evaporate this rapidly in a tared beaker or wide-necked flask to a volume of about 5 cc. Add 5 cc. of chloroform to the residue and set it aside in a moderately warm place. When the solvent has all evaporated add to the crystals 10 cc. of a mixture of equal volumes of dehydrated alcohol and purified petroleum benzine, which has previously been saturated with pure cantharidin, allow the mixture to stand for fifteen minutes, and then decant the liquid through a pledget of purified cotton. Wash the crystals with successive portions of a saturated solution of cantharidin similar to that directed above, until free from fat and colouring matter, and pass the washings through the same pledget of purified cotton. Then wash the cotton with a very small quantity of warm chloroform to dissolve any adhering crystals, collect the chloroform in the tared flask or beaker containing the washed crystals, evaporate the solvent with the aid of a blast of air, dry the crystals at 60° C. for one half-hour, and weigh. The resulting weight will be the amount of cantharidin obtained from 10 gm. of cantharides.[1]

[1] See also Eder and Schneiter, *Schweiz. Apoth. Ztg.*, 1925, **63**, 229, 245; David, *Pharm. Ztg.*, 1927, **72**, 56.

Cochineal (*Coccus*).—Consists of the dried female insects, *Coccus cacti*, enclosing the young larvæ.

Varieties.—(1) Silver grain, which retains the waxy covering of the insects and has a whitish appearance. This is the most common variety. (2) Black grain, which is dark brown in colour, the wax having been removed by killing the insects in boiling water. The silver grain variety is sometimes adulterated by fixing white and heavy powders such as barium sulphate on the insects to increase the weight. The ash should not amount to more than 6 per cent.

Colour Value.—Weigh out 0·2 gm. of the powder and shake occasionally during three hours with 50 cc. of 45 per cent. alcohol. After standing overnight shake, filter, and dilute 5 cc. to 50 cc. with water. Acidify, and either determine the colour in the 1 cm. cell of a tintometer or match against a standard sample. Not less than 5 red tintometer units should be required. The colour may also be matched against a standard ferric chloride solution (1 cc. ≡ 0·00002 gm. Fe) after adding 5 cc. of dilute hydrochloric acid and 5 cc. of potassium thiocyanate solution, and diluting to 50 cc.

Hæmoglobin.—Hæmoglobin, or more correctly Oxyhæmoglobin, occurs as reddish-brown crystals or powder, but is more usually employed as scales. It contains about 0·3 per cent. of iron. It is soluble in water, but coagulates at 64° C. Oxyhæmoglobin may be recognised by its characteristic absorption spectrum. A dilute solution is changed from a brownish colour to a cherry red on passing carbon monoxide or coal gas through the solution. *Nitrogen* content about 13 per cent.

Insulin.—Insulin is the preparation of the specific anti-diabetic principle of the pancreas. The hormone is not known in a state of purity. Commercial preparations are either in the form of a sterile solution of insulin hydrochloride or sterile tablets containing a definite amount of the hydrochloride. The solution is preserved with a small amount (about 0·3 per cent.) of pure cresol or other bactericide. The hydrogen-ion concentration of insulin solution is not less than pH=4 or greater than pH=3.[1] Insulin must be stored in containers of non-alkaline glass in order to prevent neutralisation and consequent precipitation of the insulin. Insulin is standardised biologically against a standard preparation held by the National Institute for Medical Research. The unit of insulin is the specific activity given by 0·125 mg. of the standard preparation.

Lecithin.—Commercial lecithin is a translucent, wax-like substance, soluble in ether-alcohol, from which it is precipitated by acetone. The ash varies from traces up to about 8 per cent. The moisture content should not be more than 5 per cent.

Phosphorus.—About 0·5 gm. is ignited with 2·5 gm. of fusion mixture until completely oxidised and fused. The residue is dissolved in dilute hydrochloric acid, and the phosphate determined by precipitation with magnesia mixture in the usual manner. Lecithin, when pure, contains 4 per cent. of phosphorus; percentage $Mg_2P_2O_7$ found × 7·27 = lecithin per cent.

Nitrogen is determined by Kjeldahl's method. Pure lecithin contains 1·8 per cent. of nitrogen. Any disturbance in the nitrogen-phosphorus ratio

[1] Therapeutic Substances Regulations, 1927, under the Therapeutic Substances Act, 1925.

shows the presence of phosphatides other than lecithin, but these are usually present in commercial samples.

Pancreatin.—Pancreatin occurs as a cream-coloured powder with a slight but not offensive odour. It is partially soluble in water.

Active Constituents.—The enzymes *amylase*, *trypsin*, and *lipase*. The U.S.P. requires that it should convert not less than 25 times its own weight of starch into soluble carbohydrates under the conditions of the following test: Shake 10 gm. or more of powdered potato starch with about 10 times its weight of cold distilled water, and after draining the mixture on a filter, wash it with the same quantity of distilled water. Place the washed starch at once in an air bath and maintain a temperature of about 50° C. until the starch is sensibly dry. Reduce it to a fine powder, and place it in a well-stoppered bottle. Determine the percentage of water still remaining in the starch by drying about 0·5 gm. of it in an air-bath, gradually raising the temperature to 120° C. and maintaining it at that temperature for four hours. Of the washed and partially dried starch mix a quantity equivalent to 7·5 gm. of dry starch in a 400 cc. beaker with 10 cc. of cold distilled water, and 190 cc. of boiling distilled water, and boil the mixture gently for approximately five minutes with constant stirring, until a translucent uniform paste is obtained. Replace the water lost by evaporation and cool the paste to 40° C. in a water bath previously adjusted to this temperature, and add a solution of 0·3 gm. of pancreatin in 10 cc. of distilled water, just previously heated to 40° C. Mix well, and maintain the same temperature for exactly five minutes, when a thin, nearly clear liquid is produced. At once add 0·1 cc. of this liquid to a previously made mixture of 0·2 cc. of tenth-normal iodine and 60 cc. of distilled water; no blue, red, or violet colour is produced.

Proteolytic Power.—The U.S.P. gives the following test for casein digestive power: Place 0·1 gm. of finely powdered casein in a 50 cc. volumetric flask, add 30 cc. of distilled water, and shake well to bring the casein into suspension. Add exactly 1 cc. of *N*/10 sodium hydroxide, and heat the mixture at 40° C. until the casein is completely dissolved, which should not require more than thirty minutes. Cool, add sufficient distilled water to make 50 cc. and mix well. Dissolve 0·1 gm. of pancreatin in 500 cc. of distilled water. Mix 1 cc. of glacial acetic acid with 9 cc. of distilled water and 10 cc. of alcohol. Place 5 cc. of the casein solution in a test-tube, add to it 2 cc. of the well-shaken pancreatin solution and 3 cc. of distilled water, and mix by gentle agitation. Immediately immerse the test-tube in a water bath at 40° C., and keep it at this temperature for one hour. Then remove from the bath and add 3 drops of the acetic acid mixture. No precipitate is produced. The following method is more useful as a method of comparison: A 4 per cent. solution of casein is prepared, making neutral to thymol-blue before making up to volume. A 1 per cent. pancreatin solution is prepared by triturating 1 gm. in a mortar with a little chloroform water and making up to 100 cc. After standing one hour it is used unfiltered. Neutral formaldehyde solution is prepared by mixing 1 cc. thymol-blue solution with 50 cc. of 40 per cent. formaldehyde solution and adding *N*/10 solution of sodium hydroxide until just blue. 25 cc. of the casein solution are mixed with 5 cc. of the pancreatin solution and diluted to 50 cc.; 20 cc. are removed, mixed with 10 cc. of formaldehyde, and titrated immediately with *N*/10 sodium hydroxide to thymol blue to a green colour.

The remainder is allowed to digest at 55° C. for twenty minutes, after which 20 cc. (=0·02 gm. pancreatin) are removed and mixed with 10 cc. of neutral formaldehyde solution. Titrate to thymol blue to the same end-point as the control. Subtract the number of cc. used in the control and express result as the number of cc. of $N/10$ sodium hydroxide per 1 gm. of pancreatin. A result of not less than 200 should be obtained.

Pepsin.—Pepsin is an enzyme obtained from the stomach of the pig, sheep, or calf. It occurs as nearly colourless or yellow, transparent scales or a fine cream-coloured powder soluble in water to a slightly acid solution. The B.P. requires that it should digest 2500 times its weight of coagulated white of egg in six hours when tested as follows: Prepare some coagulated white of egg by boiling fresh eggs in water for fifteen minutes, immersing them in cold water until cool, separating the whites, at once rubbing these through a hair-sieve having 12 meshes to a centimetre, and using the product before it has lost moisture by evaporation. Prepare also a pepsin solution by triturating 0·25 gm. of the pepsin with 1 gm. of sodium chloride in a small mortar until thoroughly mixed, adding by degrees acidified water (prepared by diluting 6·5 cc. of hydrochloric acid to 1000 cc. with water), continuing the trituration, transferring to a litre flask, washing the mortar with acidified water, and adding the washings to the contents of the flask until 1000 cc. are produced, then shaking frequently during six hours, and again immediately before use. Introduce 20 cc. of the pepsin solution so prepared into a 250 cc. flask. Triturate 12·5 gm. of the freshly prepared coagulated white of egg in a small mortar with 50 cc. of acidified water until reduced to uniform granules. Transfer to the flask, rinsing the mortar with a further 50 cc. of acidified water, adding the rinsing to the contents of the flask. Immerse the flask in a water bath so that its contents are on a lower level than the water in the bath, and digest at a temperature between 40° and 41° C. for six hours, shaking at intervals of fifteen minutes. For the comparative valuation of samples of pepsin the following test is useful. In each of five 200 cc. conical flasks are placed 100 cc. of a clear, filtered, 1 per cent. albumen solution; 10 cc. of N hydrochloric acid are added to each. Two flasks serve as controls and are heated for fifteen minutes in a boiling water-bath after addition of 10 cc. of saturated sodium chloride solution; when cold, the coagulated mass is collected on a dried, weighed filter, washed free from chlorine, pressed and dried to constant weight. The mean of the two is taken as the total albumen. To the contents of the three other flasks, heated to 55° C., are added different quantities of a 3 per cent. solution of pepsin, or the same quantity of solutions of different samples of pepsin. 0·1 gm. of pepsin should not be exceeded. The flasks are shaken once and kept for two hours at 55° C. exactly; after the addition of 10 cc. of sodium chloride solution they are heated for thirty minutes in boiling water, cooled, filtered, etc., and weighed as before. The difference in weight from the control gives the dissolved albumen.

Peptone.—Commercial peptone is a digestion product from various kinds of protein material, such as meat, blood fibrin, casein, etc. It consists of a mixture of proteoses, peptone, and amino acids. Peptone for bacteriological purposes should be free from sugars, and almost completely soluble in water. For some purposes the peptone should contain a high proportion of proteose and little amino acid, but for other purposes it is preferred with a high amino acid content and little or no proteose.

Ash.—This consists chiefly of sodium chloride and should be as low as possible.

Total Nitrogen should be about 12 per cent.

Proteose Nitrogen may be determined by saturating with zinc sulphate, filtering off the precipitate, washing with saturated zinc sulphate solution, and determining the nitrogen in the precipitate by the Kjeldahl method.

Amino-acid Nitrogen (Formaldehyde figure).—Take 10 cc. of formaldehyde solution; add 1 cc. of phenolphthalein solution and $N/5$ barium hydroxide solution until slightly pink. Add this to 1 gm. of peptone in 20 cc. of water (previously neutralised to phenolphthalein) and titrate with $N/5$ baryta solution until distinctly red (not pink). Express the result as the number of cc. of $N/10$ alkali for 1 gm. of peptone.

Insoluble matter should not exceed 3 per cent.

Pituitary (Posterior Lobe) Extract.—This is the watery extract prepared from the separated posterior lobe of the pituitary body. It is used in the form of a sterile solution. The hydrogen-ion concentration is not less than that corresponding to $p\mathrm{H}=5$ or greater than that corresponding to $p\mathrm{H}=4$.[1] Pituitary extract is standardised biologically against a standard sample kept by the National Institute for Medical Research.

Thyroid Gland.—An important active constituent of the thyroid gland is thyroxin, a compound containing 65·3 per cent. of iodine. Dried thyroid gland is often standardised to a definite content of total iodine, but it should be pointed out that the iodine content is not a measure of the thyroxin content, since other iodine compounds are present. Dried thyroid gland (*Thyroideum Siccum*, B.P.; *Thyroideum*, U.S.P.) is a yellowish, amorphous powder. The B.P. preparation is not standardised, but the U.S.P. is required to contain not less than 0·17 and not more than 0·23 per cent. of iodine in organic combination. The P.G. requires not less than 0·18 per cent. of iodine. The moisture should not be more than 6 per cent. and the ash not more than 5 per cent. (U.S.P.).

Determination of Iodine.—Numerous methods have been proposed; the following, due to Kendall,[2] as modified by Kelly and Husband,[3] gives good results. Weigh 0·5 gm. of thyroid gland or 0·1 gm. of dried gland into a nickel crucible 5 cm. in diameter, and cover with 10 cc. of 40 per cent. sodium hydroxide solution. Heat in an oven for half an hour, then place in a larger nickel crucible half-filled with sand and heat gently until frothing ceases, stirring with a nickel rod. Add 5 gm. of solid sodium hydroxide in powder, then small quantities of potassium nitrate until all the carbon is oxidised, and no further bubbling occurs. Too long heating is to be avoided. Cool, and extract the melt in a 500 cc. beaker with boiling distilled water. Filter if necessary and transfer the filtrate to a 700 cc. conical flask. Run in syrupy phosphoric acid from a burette until neutral to methyl red, then add a further 2 to 3 cc. of acid in excess. Boil for fifteen to twenty minutes, add 2 cc. of 20 per cent. sodium bisulphite and boil to expel the excess of sulphur dioxide, adding fragments of porous pot to prevent bumping. Care should be taken not to let the volume get too low. On cooling, add 5 to 10 drops of bromine and shake until the bromine colours the solution

[1] Therapeutic Substances Regulations, 1927, under the Therapeutic Substances Act, 1925.

[2] *J. Biol. Chem.*, 1920, **43**, 149.

[3] *Biochem. J.*, 1924, **18**, 951.

brown. Boil again for fifteen minutes to expel the bromine, add a pi of salicylic acid, remove the porous pot and cool. Dissolve a small crystal (0·25 gm.) of potassium iodide in 20 cc. of water and add to the liquid. Titrate the liberated iodine with $N/200$ sodium thiosulphate to starch. Then—

$$\frac{\text{No. of cc. of thiosulphate used} \times \text{iodine equivalent of thiosulphate solution}}{6}$$

=total iodine in amount of substance taken.

Pickworth[1] gives the following method: Weigh 0·25 gm. of finely powdered, dry thyroid into a nickel crucible of 150 cc. capacity. Add 10 cc. of 50 per cent. sodium hydroxide solution (free from nitrate and chloride), and mix. Cover with a lid having a $\frac{1}{8}$-in. hole in the centre and heat slowly until the water is evaporated, then heat in an oven hot enough to give a clear fusion product in about an hour (no potassium nitrate must be added). Heat rapidly over a flame to a dull red heat for a half to one minute. Cool, add about 70 cc. of water, and place on a warm plate for about an hour; stir gently until dissolved; transfer to a 250 cc. conical flask, add 3 drops of 10 per cent. sodium sulphite solution; acidify with 50 per cent. sulphuric acid from a burette, using about 13 cc., add 3 cc. in excess, cool, and add 5 cc. of $N/10$ permanganate; after three minutes add a suspension of animal charcoal purified by acid[2]; when decolorisation is complete, filter through a suction filter until bright and colourless, wash with a little water, and add a crystal of potassium iodide. Titrate immediately with $N/100$ thiosulphate. Then—

No. of cc. thiosulphate × 85 gives mgm. of iodine in 100 gm. of dried gland when 0·25 gm. is taken for the analysis.

Trypsin.—A proteolytic enzyme secreted by the pancreas. It occurs as a cream-coloured powder, almost entirely soluble in water.

Proteolytic Power.—Commercial trypsin is tested by the method given under Pancreatin, using a 0·5 per cent. solution of trypsin instead of a 1 per cent. solution of pancreatin. The value obtained should not be less than 400.

[1] *Biochem. J.*, 1925, **19**, 768.

[2] The amount required is that which will reduce 5 cc. of acidified $N/10$ permanganate in not less than five or more than twenty minutes.

SECTION III.

MISCELLANEOUS PHARMACEUTICAL MATERIALS.

Acacia, or Gum Arabic, occurs in rounded, yellowish or almost white, opaque masses. They are very brittle, and the fractured surface has a shining, vitreous appearance. Acacia should be almost entirely soluble in water (limit of insoluble matter, 0·2 per cent.), forming a transparent solution which is feebly acid to litmus. 0·2 cc. of lead acetate solution added to 10 cc. of a 10 per cent. solution of the gum should give no precipitate. A solution of 1 in 1 strength should not form a glairy mucilage, nor on diluting should a gummy deposit be thrown down, showing the absence of inferior gums. Inferior gums usually contain tannin, which may be detected by the addition of ferric chloride. Powdered gums may be adulterated with dextrin or starch, which may be detected by the brown or blue colour produced with iodine. Pure acacia shows slight lævo-rotation, so that a dextro-rotation will also indicate the presence of dextrin. The moisture in acacia usually amounts to 10 to 13 per cent. and the ash should not be more than 4 per cent.

Caramel (*Saccharum Ustum*).—Caramel for pharmaceutical purposes should be a dark-brown, viscous liquid, entirely soluble in water and in 60 per cent. alcohol. According to the purpose for which it is required it should not be precipitated by dilute organic acids or by dilute sodium carbonate solution. Moisture should not exceed 30 per cent. and ash should be not more than 5 per cent. The ash should be free from copper and lead.

Extract.—10 gm. are dissolved in water, made up to 100 cc., filtered, and the S.G. of the solution taken at 15° C. This is usually about 1·025.

Colouring Power.—10 cc. of the extract are diluted to 500 cc. and the colour of the solution compared with a standard sample in Nessler cylinders or by means of a tintometer.

Casein.—Edible casein occurs as a slightly yellowish powder, granules, or flakes free from objectionable or sour odour. It is sometimes rendered soluble by the addition of sodium carbonate, in which case it should form a slightly milky solution on mixing with water.

Solubility.—Insoluble, edible casein should pass the following test for solubility in borax: 15 gm. of the casein, in No. 40 powder, when stirred with 100 cc. of borax solution (76·32 gm. crystallised borax per litre) at 30° C., should form a smooth, mucilaginous solution after fifteen minutes. Moisture is determined by drying at 100° C.

Ash.—Ordinary edible casein contains from 2·5 to 4 per cent. The

soluble variety may contain more owing to the sodium carbonate added. Shaw[1] suggests moistening 3 gm. of the sample with 5 cc. of calcium acetate solution (yielding 0·15 gm. CaO per 5 cc.), drying and igniting, afterwards subtracting the weight of CaO from the ash.

Fat.—1 gm. is shaken for fifteen minutes with 10 cc. of water; 2 cc. of ammonia are added, followed after ten minutes by 10 cc. of 95 per cent. alcohol. The fat is extracted with a mixture of equal parts of ether and petroleum ether as in the Rose-Gottlieb method. The fat varies according to the method of preparation used.

Lactose.—10 gm. are dissolved in water, made acid with acetic acid, and a solution of 2 gm. sodium acetate and 1 gm. mercuric chloride is added. After mixing to a thin cream the mixture is transferred to a 100 cc. flask and made up to 100 cc. with water. After standing overnight, 50 cc. are filtered off, and sufficient zinc dust is added to precipitate the whole of the mercury. The liquid is boiled, filtered, cooled, and made up to 50 cc. 10 cc. of the filtrate are boiled with 25 cc. of Fehling solution made up to 100 cc. with distilled water. Not more than a very slight precipitate of copper oxide should be observed.

Nitrogen is estimated by Kjeldahl's method. $N \times 6{\cdot}38$=actual casein.

Diastase.—Commercial malt diastase is a yellowish-brown powder, partially soluble in water. The diastatic value may be determined in the same way as for Malt Extract (p. 232), using 10 cc. of a 0·2 per cent. solution of the diastase. The diastatic activity$=\frac{25{,}000}{xy}$ where x=no. of cc. of solution in 100 cc. of fully diluted starch conversion liquid and y=no. of cc. used to reduce 5 cc. of Fehling solution. If the result exceeds 500 the determination must be repeated using a smaller amount. U.S.P. IX. required that diastase should convert not less than 50 times its weight of potato starch into sugars.

Gelatine occurs in thin sheets, colourless, or nearly colourless in the best grades. Cheaper varieties such as are used for capsules, etc. are yellowish in colour. The ash content should not be more than 2 per cent. (B.P.). The B.P. states that "a solution in hot water (1 in 50) is inodorous and solidifies to a jelly on cooling. An aqueous solution yields a precipitate with solution of tannic acid, but not with solutions of other acids or with dilute solution of alum, solution of lead acetate, or ferric chloride." Heavy metals may be tested for in the ash.

Sulphur Dioxide.—20 gm. of gelatin are dissolved in 150 cc. of hot water and distilled with steam after the addition of 5 cc. of phosphoric acid, the distillate being collected in a flask to which is attached an absorption bulb containing 25 cc. of $N/10$ iodine solution. A second absorption bulb connected to the first contains potassium iodide solution to absorb any iodine which may be carried over. When 50 cc. of distillate have been collected, wash the contents of the bulbs into the flask containing the distillate, acidify with hydrochloric acid, precipitate the sulphate with barium chloride, and weigh the $BaSO_4$ in the usual way. $SO_2=BaSO_4 \times 0{\cdot}2744$. The U.S.P. limit for sulphur dioxide is 0·002 per cent., but for gelatine required for use in making capsules 0·15 per cent. is allowed. The Public Health Regulations limit the amount of sulphur dioxide to 0·1 per cent.

Honey (*Mel Depuratum*, B.P.).—Purified honey for official preparations,

[1] *J. Ind. Eng. Chem.*, 1920, **12**, 1168.

is commercial honey melted and strained, the S.G. being adjusted to 1·36. Honey differs in its properties according to the country of origin.

Optical Rotation.—According to the B.P. a 25 w/v solution should give a rotation in a 200 mm. tube of 0° to −5°. The U.S.P. merely requires honey to be lævo-rotatory. Many natural honeys are more strongly lævo-rotatory than the B.P. limit,[1] some being as high as −12°. Occasionally, honeys, especially those from Hawaii, are slightly dextro-rotatory. The ash should not be more than 0·3 per cent. If this figure is exceeded the ash should be tested for calcium sulphate, which indicates glucose syrup.

Invert Sugar.—Place 10 cc. of a 50 per cent. solution in a test-tube, add 5 cc. ether, shake, and allow to stand until the ether is clear. Transfer 2 cc. of the ether to a small test-tube, add 1 drop of a 1 per cent. solution of resorcin in hydrochloric acid, and shake. A cherry-red colour indicates commercial invert sugar. A faint orange or rose tint may be due to heating of the honey.

Isinglass.—Isinglass consists of fibres or threads of collagen obtained from the swimming bladder of the sturgeon and other fishes. The Russian variety is the most valued, the commoner kind being chiefly obtained from Brazil. Isinglass swells up in cold water, but retains its shape. It dissolves in hot water, the better kinds almost entirely; the commoner kinds leave varying amounts of insoluble matter. The solution should have not more than a faint odour if the isinglass is of good quality, and should set to a jelly on cooling. Moisture, 15 to 20 per cent. Ash—Russian, 0·4 to 0·9 per cent.; Brazil, up to 2 per cent. Nitrogen, about 18 per cent. Isinglass may be adulterated with gelatin.

Malt Extract (*Extractum Malti*).—Malt extract is an aqueous extract from malt evaporated *in vacuo* to the consistency of a thick syrup. S.G. about 1·44.

Total Solid Matter.—Determine the S.G. of a 10 w/v solution at 15° C.

Then total solids per cent. $= \frac{(\text{S.G.} - 1)10{,}000}{3 \cdot 86}$.

Diastatic Value.—A 2 per cent. solution of soluble starch is prepared by dissolving 5 gm. of soluble starch in 200 cc. of boiling water; the liquid is cooled with stirring to avoid skin formation and transferred to a 250 cc. graduated flask, washing out the beaker with water. 5 cc. of "acetate buffer solution" are added, and the liquid is made up to 250 cc. 100 cc. of this solution are transferred to a 200 cc. flask, warmed to 70° F., and hydrolysed with 10 cc. of the 10 per cent. solution of the extract at 70° F. (21° C.) for one hour. 20 cc. of $N/10$ sodium hydroxide solution are then added and the liquid cooled to 60° F., made up to 200 cc., shaken, and titrated against 5 cc. of Fehling solution. The latter is accurately measured into a 150 cc. flask and brought to the boil. The sugar solution is run in until nearly all the blue colour is destroyed. 5 drops of methylene blue solution are added, and the titration continued until the blue colour disappears. Diastatic value (° Lintner) $= \frac{500}{xy}$, where x = no. of cc. of solution in 100 cc. of fully diluted starch conversion liquid (in this case 5) and y = no. of cc. required to reduce 5 cc. of Fehling solution. If the result exceeds 50, the determination must be repeated with a smaller amount of the extract. A blank titration is carried out with 10 cc. of the solution of the extract

[1] Caulkin, *Pharm. J.*, 1927, 118, 544.

diluted to 200 cc., and the Lintner value due to this subtracted from the result.

Nitrogen is estimated by the Kjeldahl method.

Carbohydrates.—The proportions of the individual carbohydrates present in malt extract vary considerably according to the method of preparation—temperature of mashing, etc. The only likely addition is glucose syrup, which can only be detected by a careful study of the results obtained by fermentation with different strains of yeast.[1]

The usual method for analysis of malt extract is to determine the optical rotation and copper-reducing power of a 10 per cent. solution and to calculate the results as dextrin and maltose. This method, though it may be useful for control purposes, fails to take into account the presence of dextrose and lævulose, which are found in considerable amounts, and gives no real information as to the proportions of the individual carbohydrates present.

Resin (Rosin or Colophony).—This is the residue left after the distillation of the oil of turpentine from the crude oleo resin from various species of pine. For pharmaceutical use resin should be pale in colour, and entirely soluble in 90 per cent. alcohol, ether, benzene, or carbon disulphide. The ash is negligible. Acid value, 150 to 180.

Sherry (*Vinum Xericum*).—Sherry should contain not less than 16 v/v of absolute alcohol (B.P.). The B.P. requires that it shall contain not less than 0·1 or more than 0·2 w/v of volatile acids calculated as acetic acid, and not less than 0·3 or more than 0·45 w/v of fixed acids calculated as tartaric acid.

Total Acidity.—2·5 cc. of the wine are quickly heated to boiling and titrated quickly with $N/2$ NaOH, using phenolphthalein as indicator. The acidity is calculated as tartaric acid.

Volatile Acid.—50 cc. of the wine to which phosphoric acid has been added are distilled in a current of steam until 200 cc. have been collected. This quantity is titrated with $N/10$ sodium hydroxide to phenolphthalein and the acidity calculated as acetic acid. The total acidity as tartaric acid less the volatile acidity as acetic acid $\times 1{\cdot}25 =$ fixed acid as tartaric acid.

Salicylic Acid.—See Orange Wine (p. 281).

Soap.—The B.P. mentions three soaps, viz. *Sapo Animalis* (Curd Soap), made from sodium hydroxide and purified animal fats consisting chiefly of stearin; *Sapo Durus* (Hard Soap), made from sodium hydroxide and olive oil; *Sapo Mollis* (Soft Soap), made from potassium hydroxide and olive oil.

Water.—Dissolve about 0·5 gm. of soap in 10 cc. of alcohol and evaporate to dryness on the water bath in a tared dish containing 1 gm. of clean, ignited sand. Dry to constant weight at 110° C. Curd soap and hard soap should not contain more than 30 per cent. of water.

Free Alkali and Fatty Acids.—5 gm. of soap are dried, powdered, and dissolved in 50 cc. of boiling 90 per cent. alcohol. The solution is filtered hot, the filter being thoroughly washed with boiling alcohol. The filtrate should not be alkaline to phenolphthalein. If it is so, it is titrated with $N/10$ HCl, and the results calculated to free caustic alkali as Na_2O or K_2O. 1 cc. $N/10$ HCl $\equiv$ 0·0031 gm. $Na_2O \equiv$ 0·00471 gm. K_2O. If the alcoholic solution is appreciably acid to phenolphthalein, *free fatty acids* are present and may be titrated with $N/10$ KOH, and calculated as oleic acid. 1 cc. $N/10$ KOH $\equiv$ 0·0282 gm. oleic acid. The residue on the filter

[1] McLachlan, *Analyst*, 1928, **53**, 583.

paper is washed with hot water, and the washings titrated with $N/10$ a to methyl orange; the result is calculated as Na_2O or K_2O and returr as free alkali (carbonate). The B.P. requires that 5 gm. of dried ε powdered soap should require not more than 5 cc. of $N/10$ H_2SO_4, whicl equivalent to about 0·22 per cent. of Na_2O, or 0·33 per cent. of K_2O on original soap, allowing for 30 per cent. moisture.

Total Alkali and Fatty Acids.—5 gm. are dissolved in hot water, wasl into a separator, and 25 cc. of $N/2$ HCl are added and a few drops of met orange. After thoroughly shaking and keeping hot until the fatty ac have separated in a clear layer, the liquid is allowed to cool. The fa acids are then extracted by four treatments, each with 25 cc. of ether. ' ether is evaporated off and the residue of fatty acids dried at 100° C. ε weighed. The aqueous liquid is titrated with $N/2$ KOH, and the num of cc. of $N/2$ acid used up calculated to total alkali as Na_2O or K_2O. 1 $N/2$ KOH ≡ 0·0155 gm. Na_2O ≡ 0·02355 gm. K_2O.

Iodine Number of Fatty Acids.—This is determined in the usual man

	Average Iodine Number for Fatty Acids.
Coconut Oil	9·7
Stearin	55
Olive Oil	86
Linseed Oil	179 to 210

Tragacanth.—This is the gummy exudation obtained by incision fı *Astralagus gummifer* and some other species of *Astralagus.* Tragaca occurs in white or pale yellowish-white, thin flakes. It is partly solı in water, swelling to a gelatinous mass on standing and finally forn a mucilage. The ash content should be not more than 4 per cent. (B. Tragacanth often contains starch, and the mucilage is tinged blue b few drops of $N/10$ iodine solution.

Determination of Jelly Strength.[1]—A comparison of the jelly strer of tragacanth mucilages may be made in the following manner, wl depends on observing the time taken by a steel ball $\frac{5}{32}$ in. in diamete fall through a measured distance in the mucilage. The mucilage is prepε according to the B.P. directions, and warmed for an hour on the water l in a flask with an air condenser. It is then poured into a 50 cc. Neε cylinder and allowed to stand overnight. A cardboard scale, 5 in. in len is prepared with marks at distances of 1½ in. and 4 in. from the top e This is placed against the cylinder so that the top edge is in a line with surface of the mucilage, and so that the falling of the steel ball caı readily observed. Care should be taken that no air bubbles are pre when the determination is made. A steel ball, $\frac{5}{32}$ in. in diameter, is ı released on the surface of the mucilage with a small pair of forceps, by means of a stop-watch the time which elapses between the lower ı of the ball touching the upper and lower marks on the scale is obser The temperature should be between 15° and 20° C. Good gums will

[1] Evers and McLachlan, *Y.B.P.*, 1927, 637.

times of fall of from 150 to 300 seconds. The mucilage should be made with a powder which passes through a No. 30, but is retained by a No. 60 sieve. This suspending power of samples of tragacanth may also be compared by mixing 100 cc. of a B.P. mucilage with a suspension of 8 gm. of bismuth carbonate in 500 cc. of chloroform water. After thoroughly shaking, portions of the suspensions are poured into stoppered cylinders or flat glass bottles, and the comparative heights of the bismuth carbonate layers after standing overnight give an indication of the suspending powers of the gums. Tragacanth deteriorates on storage. The appearance of commercial samples is no indication of the relative jelly value.[1]

Vinegar.—Vinegar in this country should be prepared by the acetous fermentation of sugars derived from barley or other cereals. In a report by Dr. J. M. Hamill, issued by the Local Government Board (now the Ministry of Health) in 1908, it was stated that vinegar should contain at least 4 per cent. of acetic acid. It should be free from sulphuric or other mineral acid, lead, or copper, nor should it contain any foreign substance or colouring matter except caramel. In France vinegar is largely made from wine; in the U.S.A. from cider. The addition of acetic acid derived from wood spirit, etc. is not justifiable, and such a product should not really be sold as vinegar—if described as malt vinegar the substance is undoubtedly adulterated. A malt vinegar will give the following average results:—

S.G.	1·02
Acetic Acid	5·5 per cent.
Total Solids	2·5 " "
Ash	0·5 " "
P_2O_5 in the Ash	0·08 " "
Nitrogen	0·08 " "

Where the vinegar has been diluted with water to an amount not below 4·0 per cent. the other ingredients should be less in proportion. Acetic acid derived from wood spirit contains no nitrogen, P_2O_5, or solids, so that an artificial vinegar is determined by the absence or deficiency of these factors. The interpretation is not always easy, as some brewed vinegars give abnormally low results for these constituents.[2]

Determination.—S.G. and Nitrogen as usual.

Acetic Acid.—Place 10 cc. of the vinegar in a porcelain dish, dilute with water, and titrate with $N/2$ (or $N/10$) NaOH using phenolphthalein 1 cc. $N/2$ NaOH $\equiv$ 0·03 gm. acetic acid. Standard not less than 4 per cent.

Total Solids.—Measure 5 cc. into a porcelain or platinum dish, evaporate to dryness, and dry in oven until constant in weight.

Ash.—Add a further 20 cc. of vinegar to the dry solid, evaporate as before, ignite at a low temperature, and weigh.

P_2O_5 in the Ash.—Dissolve the ash in 25 cc. of 30 per cent. nitric acid add 15 gm. of ammonium nitrate and 20 cc. of water, and heat to 65° C Then add 20 to 30 cc. of molybdate solution, and allow to stand in a warm

[1] See also Evers and McLachlan, *Pharm. J.*, 1927, **118**, 746; Middleton, *Pharm. J* 1927, **118**, 727.

[2] *Cf.* Chapman, *Analyst*, 1912, **37**, 123.

place several hours. Filter (test filtrate with more molybdate solu allowing to stand), and wash with a 10 per cent. ammonium nitrate solu Dissolve the precipitate on a filter with 2 per cent. ammonia and filter (keep volume below 100 cc.). Add hydrochloric acid till only alkaline (yellow colour on adding acid just disappears on shaking), the magnesia mixture (10 cc. for each 0·1 gm. P_2O_5) drop by drop, with con shaking, and allow to stand fifteen minutes. Add 20 cc. of a 10 per ammonia solution, and allow to stand twelve hours. Filter, wash 2 per cent. ammonia, ignite, and weigh. ($P_2O_5 \equiv Mg_2P_2O_7 \times 0{\cdot}638$.)

PART V.

GALENICALS.

SECTION I.

AQUÆ.

The "Waters" of the British Pharmacopœia are made either by distillation of the drug with water or by solution in distilled water. They should be free from more than traces of non-volatile residue and should have the appropriate odour and taste.

"Concentrated waters" are sold for the purpose of preparing Aquæ extemporaneously. They are usually solutions of essential oils in alcohol.

Distilled Water is required by the B.P. to have the following characteristics: "Colourless, odourless, and tasteless. Yields no reactions for sulphates, chlorides, or nitrates. 100 cc. evaporated to dryness on a water bath should leave not more than 0·005 gm. of solid residue." (This is a very lenient standard for solid matter as many natural waters contain less than this.) Lead, copper, and iron should be absent. 250 cc. with 3 cc. of strong sulphuric acid and 0·1 cc. of $N/10$ potassium permanganate, after standing for three hours at about 15·5° C., should be coloured blue on the addition of a crystal of potassium iodide and a little mucilage of starch. Ammonia (by direct determination with Nessler solution) should not exceed 1 part in ten millions.

Cherry-laurel Water (*Aq. Laurocerasi*) is prepared by distillation from the leaves of the cherry-laurel. It contains hydrocyanic acid and benzaldehyde; it is required to contain 0·1 per cent. by weight of hydrocyanic acid. The B.P. allows the addition of hydrocyanic acid in order to bring it up to this strength.

Determination of Hydrocyanic Acid, B.P. (1898 method).—50 cc. of the water, made alkaline with 5 cc. of 5 per cent. potassium hydroxide solution, with 3 drops of potassium iodide solution added, are titrated with $N/10$ silver nitrate until a permanent precipitate is obtained. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·005406 gm. HCN. It must be ascertained that chlorides are absent before accepting the result. The B.P. 1914 method is not reliable. The pH value of cherry-laurel water should be about 5.

Ether Extract.—Extract 100 cc. of the water three times with ether, evaporate the ether at a low temperature, dry in a desiccator over sulphuric acid, and weigh. Not less than 0·2 per cent. should be obtained.[1]

Orange Flower Water (*Aq. Flor. Aurant*) and **Rose Water** (*Aq. Rosæ*) are liable to contain lead and copper; they should be tested, therefore, for these metals, from which they should be reasonably free.

[1] Caines, *Y.B.P.*, 1922, 419.

SECTION II.

EXTRACTS.

The extracts included in this section are the soft extracts made by evaporation to a semi-solid consistency and the dry extracts made by evaporation to dryness, usually with the addition of some inert material in order to produce a dry powder. Wokes[1] has shown that certain extracts, especially those of Belladonna and Hyoscyamus, are so hygroscopic that sufficient water may be absorbed if they are stored under certain conditions to have a marked effect on the alkaloidal content. All determinations of alkaloidal content should, therefore, be accompanied by moisture determinations.

Ext. Aconiti.—This may be assayed by the U.S.P. IX. method.[2] 3 gm. mixed with 10 gm. of washed sand are shaken in a flask with 150 cc. of ether and 2 cc. of ammonia solution every few minutes during half an hour. After allowing to settle, 100 cc. of the clear liquid (=2 gm. of extract) are decanted off into a separator through a plug of cotton-wool. The cylinder and cotton-wool are rinsed with a little ether. The alkaloids are then completely extracted by shaking several times with $N/10$ sulphuric acid. The mixed acid solutions are made alkaline with ammonia and the alkaloids extracted by shaking with several portions of ether. The ether is then distilled off and the residue dissolved in 10 cc. of $N/20$ sulphuric acid. The solution is then titrated with $N/20$ sodium hydroxide solution to methyl red. 1 cc. $N/20$ $H_2SO_4 \equiv 0{\cdot}03227$ gm. ether-soluble alkaloids. The U.S.P. IX. powdered extract is required to contain 1·8 to 2·2 per cent. ether-soluble alkaloids. *Ext. Aconiti* B.P. '85 is made from the herb and is much weaker.

Ext. Belladonnæ Siccum, B.P. (*Ext. Belladonnæ Alcoholicum,* B.P.)—Standard: 1 per cent. $\pm 0{\cdot}05$ per cent. of alkaloids.

Determination of Alkaloids.—Slightly moisten 5 gm. with a mixture of 1 vol. of acetic acid (B.P.) and 9 vols. of alcohol, 70 per cent.; pack in a small percolator and percolate until 50 cc. have been collected. Evaporate to about 10 cc., add sufficient 90 per cent. alcohol to dissolve any separated substance, and transfer to a separator, rinsing the dish with a little water. Add 10 cc. of water, 20 cc. of chloroform, and sufficient ammonia solution to make alkaline. Shake well and separate the chloroform layer. Repeat the extraction with two 10 cc. quantities of chloroform. Shake out the mixed chloroform solutions with 10 cc. of N sulphuric acid diluted with

[1] *Y.B.P.*, 1926, 396.

[2] For criticisms of the methods for the assay of *Ext. Aconiti*, see Cornwell and Jones, *Y.B.P.*, 1926, 388.

20 cc. of water. Separate, and again extract the chloroform solution with a further 10 cc. of the acidified water. To the mixed acid solutions add 20 cc. of chloroform and 4 cc. of ammonia solution. Shake thoroughly, separate, draw off the chloroform into a flask, and extract with two portions each of 10 cc. of chloroform. Distil off the chloroform from the mixed solutions and dry the residue in the steam oven for half an hour. Dissolve in 10 cc. of $N/20$ sulphuric acid and titrate back with $N/20$ sodium hydroxide to methyl red. 1 cc. $N/20$ sulphuric acid $\equiv 0{\cdot}01446$ gm. of alkaloids.

The U.S.P. method is more satisfactory. The standard is 1·18 to 1·32 per cent. of alkaloids. Digest 2 gm. with about 10 cc. of diluted alcohol (70 per cent.). Transfer to a separator containing 25 cc. of chloroform and rinse the dish thoroughly with small portions of diluted alcohol, adding the rinsings to the separator. Dilute the alcoholic liquid with a sufficient quantity of distilled water, add enough ammonia solution to make it decidedly alkaline, and completely extract the alkaloid by shaking with successive portions of chloroform. The process is completed in the same way as in the case of Belladonna Leaves (p. 188). This method is better than that of the B.P. and gives slightly higher results.

Ext. Colchici.—The B.P. preparation from the corm is not standardised, nor was *Ext. Colchici Aceticum* (B.P. '85), prepared from the seeds. The U.S.P. *Ext. Colchici Corm.* is standardised to contain 1·4 per cent. (limits, 1·25 to 1·55 per cent.) colchicine by the following method: 6 gm. are disintegrated in 290 cc. of water and 10 cc. of lead sub-acetate solution added. The vessel and contents are weighed and heated at 60° to 70° C. for three hours with occasional shaking, then cooled and sufficient water added to bring the weight up to the original. 200 cc. are filtered off, 0·75 gm. of sodium phosphate added to the filtrate, and the mixture shaken frequently during half an hour. 100 cc. (=2 gm. of extract) are filtered off. The filtrate is extracted with chloroform until on testing with iodine solution the aqueous liquid gives no precipitate. The chloroform is distilled off, 1 cc. of alcohol is added, and the liquid again evaporated. This operation is repeated and the liquid dried to constant weight at 100° C. To the weighed residue 10 cc. of $N/20$ sulphuric acid are added and the liquid warmed to 70° C. for ten minutes. It is then filtered through a plug of cotton-wool, the flask and cotton are washed with distilled water, and the filtrate and washings rejected. As much water is removed from the wool as possible and the residue dissolved with alcohol, followed by ether, in a weighed flask. The alcohol and ether are evaporated off and the residue dried at 100° C. to constant weight. This weight is subtracted from the weight of crude alkaloid. The difference $\times$ 50 = percentage of colchicine. When tested by this method the U.S.P. extract shows 1·25 to 1·55 per cent. of colchicine.

Ext. Glycyrrhizæ, see Liquorice (p. 204).

Ext. Hyoscyami, B.P., is a powdered extract prepared from hyoscyamus leaves and standardised to contain 0·3 per cent. of alkaloids. The B.P. directs that when examined as for *Ext. Bellad. Sicc.*, this extract should contain $0{\cdot}3 \pm 0{\cdot}015$ per cent. of alkaloids, but since 5 gm. of the extract would give only about 0·015 gm. of alkaloids it is better to use 10 gm. of the extract and percolate with the acid alcohol until 100 cc. have been collected. The U.S.P. method, as given under *Ext. Belladonnæ*, is more satisfactory.

Ext. Malti (see p. 232).

Ext. Nucis Vomicæ.—The B.P. preparation, *Ext. Nucis Vomicæ Siccum* (B.P.), is standardised to contain 5 per cent. of strychnine; the U.S.P. requires *Ext. Nucis Vomicæ* to contain 15·2 to 16·8 per cent. of the total alkaloids of Nux Vomica. The B.P. method of determination consists in exhausting 3 gm. of the extract with 70 per cent. alcohol and treating the liquid as for *Ext. Nucis Vomicæ Liquidum* (*q.v.* p. 243). The U.S.P. method for *Ext. Nucis Vomicæ* is the same as given under *Ext. Belladonnæ* (p. 238), using 1 gm. of the extract. 1 cc. $N/10$ acid $\equiv$ 0·0364 gm. alkaloids.

Ext. Opii.—The dry extract of opium of the B.P. (*Ext. Opii Siccum*, B.P.) is standardised to contain 20 per cent. of anhydrous morphine. The method of determination is the same as for opium, the limit of error being ± 1 per cent. of morphine. The U.S.P. IX. extract also contains 20 per cent. of anhydrous morphine, the limit of error when determined by the U.S.P. IX. method being $\pm 0{\cdot}5$ per cent. of morphine.

Ext. Physostigmatis, U.S.P. IX., is standardised to contain 2 per cent. of alkaloids. For the determination, 3 gm. are mixed with 10 gm. of washed sand, 150 cc. of ether added, and the process continued as for Physostigma (see p. 215). Limit of error $\pm 0{\cdot}3$ per cent. of alkalose.

Ext. Stramonii, U.S.P., is required to contain 0·9 to 1·1 per cent. of alkaloids, as determined by the method given under *Ext. Belladonnæ* (p. 238).

SECTION III.

LIQUID EXTRACTS.

LIQUID extracts (Fluid extracts, U.S.P.) are concentrated preparations of drugs containing alcohol as solvent or preservative and bearing a definite relation to the drug, such as that 1 cc. represents 1 gm. of the drug. For the determination of alcohol and total solid residue, see p. 265.

Ext. Belladonnæ Liq., B.P., is prepared from the root and standardised to contain 0·75 per cent. of alkaloids. S.G. about 0·920 to 0·959; alcohol content about 69 v/v.

Determination of Alkaloids, B.P.—10 cc. of the liquid extract are thoroughly shaken with 50 cc. of water, 2 cc. of dilute sulphuric acid and 10 cc. of chloroform, and allowed to separate. The lower layer is drawn off and washed by shaking with two portions each of 10 cc. of water acidified with sulphuric acid, the acid washings being added to the upper layer in the separator. The liquid is then made distinctly alkaline with ammonia and the alkaloids are extracted by shaking with three quantities each of 10 cc. of chloroform. The mixed chloroform solutions are washed by shaking with 10 cc. of water, separated, transferred to a flask, and the chloroform distilled off. After heating the residue for thirty minutes on the water bath, it is dissolved by warming with 10 cc. of $N/20$ sulphuric acid. After cooling, the solution is titrated back with $N/20$ sodium hydroxide to methyl red. 1 cc. $N/20$ sulphuric acid $\equiv$ 0·01446 gm. alkaloids of belladonna. Standard: $0{\cdot}75 \pm 0{\cdot}05$ w/v alkaloids. The U.S.P. fluid extract of belladonna root contains 0·45 w/v alkaloids. The standardisation is carried out by pipetting 10 cc. of the fluid extract with an equal quantity of water into a separator containing 25 cc. of chloroform, making alkaline with ammonia, and proceeding by the U.S.P. method given for *Ext. Belladonnæ* (p. 238). The U.S.P. fluid extract of belladonna leaves may be standardised in the same way (standard, 0·3 per cent. of alkaloids).

Ext. Cinchonæ Liq., B.P.—Standard, $5 \pm 0{\cdot}2$ w/v of alkaloids; S.G. 1·10 to 1·15; alcohol content about 12 v/v. The B.P. method of assay is as follows: To 5 cc. of the liquid extract in a separator are added 15 cc. of benzolated amyl alcohol (benzene, 3 vols.; amyl alcohol, 1 vol.) and 10 cc. of N alcoholic potassium hydroxide, and after thorough shaking the liquid is kept in a warm place with frequent shaking for some minutes. After allowing the liquids to separate, the clear upper layer is removed and the lower layer shaken with two further portions of 15 and 10 cc. of benzolated amyl alcohol. The combined alcoholic liquids are then shaken with two 5 cc. quantities of water and the washings rejected. A warm mixture of 12 cc. of dilute hydrochloric acid and 60 cc. of water is

prepared, and the alcoholic liquid extracted with successive quantities of 30, 30, and 12 cc. of the acid. The mixed acid liquids, after making alkaline with ammonia, are shaken first with 15 cc. of chloroform, then with successive portions of 10 cc. of chloroform until the aqueous liquid, after acidification, gives no precipitate with Mayer's reagent. The chloroform is then distilled off and the residue of alkaloids dried at 110° C. and weighed. The U.S P. *Fluid Ext. Cinchonæ*, which contains 4·5±0·5 w/v alkaloids, is assayed as follows: Drop 5 cc. evenly over the surface of 10 gm. of purified sawdust, and evaporate to dryness at a low temperature. Transfer the mass to a flask containing 200 cc. of ether-chloroform (3 : 1), and wash the dish with small portions of ammonia, adding the washings to the flask until a total of 10 cc. of ammonia has been added. Shake during one hour. Decant 160 cc. (=4 cc. fluid extract) and proceed as under Cinchona (p. 193), U.S.P. method.

Fluidext. Colchici, U.S.P., is standardised to contain 0·36 to 0·44 gm. of colchicine. It is assayed by placing 15 cc. of the fluid extract in a 500 cc. flask with 275 cc. of distilled water and 10 cc. of lead sub-acetate solution, and shaking frequently during an hour. 200 cc. are then filtered off and treated by the U.S.P. method for Colchicum Seeds (p. 194). *Fluidext. Colchici* contains 53 to 58 v/v alcohol.

Ext. Ergotæ Liq., B.P.—S.G. about 1·025; total solids about 16 w/v; alcohol about 30 to 33 v/v. Since *Ext. Ergotæ Liq.*, B.P., has been shown to be practically devoid of physiological activity, liquid extracts which are biologically standardised are usually made by the U.S.P. acid-alcohol extraction method or a similar process. This liquid extract should be physiologically standardised to contain 0·1 per cent. ergotoxine.

Colour Test.—Mix 2 cc. with 1 cc. of 10 per cent. ammonia and shake out with 15, 10, and 5 cc. of ether. Filter the mixed ethereal solutions and evaporate to dryness. Dissolve the residue in 15 cc. of glacial acetic acid. Filter off 4 cc. and mix with 4 cc. of 50 v/v sulphuric acid. After standing overnight a brilliant blue colour should be formed. *Fluidext. Ergotæ*, U.S.P., contains from 37 to 42 v/v alcohol.

Ext. Filicis Liq., B.P. (Liquid Extract of Male Fern).—Standard, not less than 20 per cent. filicin. S.G. not less than 1·0. Refractive index at 40° C. not less than 1·49.

Determination of Filicin, B.P.—5 gm. of the liquid extract are dissolved in 40 cc. of ether, transferred to a separator, and shaken continuously for five minutes with 100 gm. of 3 per cent. barium hydroxide solution. After separation, 86 gm. of aqueous liquid (=4 gm. of extract) are filtered off and acidified with hydrochloric acid. The filicin is then extracted with quantities of 30, 20, and 15 cc. of ether. The mixed ethereal solutions are filtered, the ether distilled off, and the residue dried at 100° C. and weighed. The weight should be not less than 0·8 gm.

Ext. Hydrastis Liq., B.P. Standard, 2±0·1 w/v hydrastine; S.G. 1·012; alcohol, about 50 v/v.

Determination of Hydrastine.—10 cc. of liquid extract in a 100 cc. graduated flask are mixed with 20 cc. of potassium iodide solution diluted with 60 cc. of water and made up with water to 100 cc. After shaking for several minutes the liquid is filtered and 50 cc. of the filtrate (=5 cc. of liquid extract) are transferred to a separator, made alkaline with ammonia, and shaken at intervals for several minutes with 30 cc. of ether. The

ether is separated and the aqueous liquid shaken with two further quantities each of 20 cc. of ether for one minute. The ether is distilled off from the mixed ethereal solutions and the residue dried on the water bath and weighed. The weight of hydrastine ×20=w/v hydrastine in the liquid extract. The U.S.P. *Fluidext. Hydrastis* (standard, 2±0·2 w/v ether-soluble alkaloids of hydrastis) is assayed as for *Fluidext. Belladonnæ Radicis* (see p. 241), using 5 cc. and ether only as the solvent.

Fluidext. Hyoscyami, U.S.P., contains 0·055 to 0·075 gm. alkaloids. It is assayed in the same way as *Fluidext. Bellad. Rad.*, using 25 cc.

Ext. Ipecac. Liq., B.P. Standard, 2±0·1 w/v alkaloids. S.G. about 0·885; alcohol about 78 v/v.

Determination of Alkaloids (B.P.).—To 5 cc. of the liquid extract in a separator add 4 cc. of water, 1 cc. of dilute sulphuric acid, and 10 cc. of ether; shake thoroughly and allow to separate. Draw off the aqueous layer and again extract with 5 cc. of ether. Wash the mixed ethereal solutions with two portions each of 5 cc. of water, and add the washings to the aqueous portions. Shake the latter with 10 cc. of chloroform and a slight excess of ammonia solution. Separate, and again extract twice with 10 cc. of chloroform. Filter the chloroform solution into a weighed flask, washing the filter paper with chloroform. Distil off the chloroform until about 2 cc. remain, add 5 cc. of ether, evaporate and dry at a temperature below 80° C. Weigh the alkaloids. *Fluidext. Ipecacuanhæ,* U.S.P., is required to contain 1·35 to 1·65 per cent. of ether-soluble alkaloids. The assay is carried out as for *Fluidext. Belladonnæ* (p. 241), using 5 cc. and ether as the solvent. 1 cc. $N/10$ acid ≡ 0·024 gm. alkaloids. The alcohol content is 28 to 33 v/v.

Ext. Kolæ Liq., B.P.C.—S.G. about 0·960; alcohol about 54 v/v.

Determination of Caffeine.—15 gm. are weighed into a dish and evaporated to about 8 gm. The residue is washed with four quantities each of 2 cc. of water into a mortar, and mixed thoroughly with 10 gm. of calcined magnesia. After standing for an hour the mixture is placed in a dry 250 cc. flask with 150 gm. of chloroform, and weighed. After boiling under reflux for forty-five minutes the flask is cooled and weighed again, and chloroform added to restore the weight. 100 gm. of the chloroform solution (=10 gm. of fluid extract) are then weighed in a flask, the chloroform distilled off, and the residue of caffeine dried at 100° C. and weighed. The fluid extract of Kola of the French Codex is required to contain not less than 1·25 per cent. of caffeine.

Ext. Nucis Vomicæ Liq., B.P. Standard, 1·5±0·05 w/v of strychnine. S.G. about 0·950; alcohol about 60 v/v.

Determination of Strychnine (B.P.).—Evaporate 10 cc. on a water bath to a syrupy extract, dissolve the residue in 10 cc. of warm water, and transfer to a separator, washing the dish with 10 cc. of water. Add 10 cc. of chloroform and 5 gm. of sodium carbonate dissolved in 25 cc. of water.[1] Shake thoroughly and allow to separate. Extract with two further quantities of 10 cc. of chloroform. Extract the alkaloids from the mixed chloroform solutions with three portions each of 10 cc. of N sulphuric acid. Make the mixed acid extracts alkaline with ammonia and again extract the alkaloids with 10, 5, and 5 cc. of chloroform. Distil off the chloroform and dissolve

[1] Dott, *Pharm. J.*, 1924, 112, 337, shows that higher results are obtained by using sodium hydroxide instead of sodium carbonate.

the residue in 15 cc. of water containing 3 per cent. by weight of sulphuric acid; heat to 50° C., add 3 cc. of a mixture of equal volumes of nitric acid and water, and set aside for exactly ten minutes. Transfer to a separator, rinsing the flask with a little water, make alkaline with sodium hydroxide solution, and extract the alkaloid by shaking successively with 10, 5, and 5 cc. of chloroform. Wash the mixed chloroform solutions in a separator with 5 cc. of water, transfer to a weighed flask, and distil off the chloroform carefully, adding 5 cc. of alcohol towards the end to prevent loss of strychnine by decrepitation. Evaporate to dryness, dry at 100° C., and weigh. Weight obtained $\times 10 =$ w/v strychnine.

Fluidext. Nucis Vomicæ, U.S.P. IX., is standardised to contain 2·5 $\pm$0·13 w/v of total alkaloids of nux vomica. The method of determination is similar to the U.S.P. method for *Fluidext. Belladonnæ Radicis* (see p. 241).

Ext. Opii Liq., B.P.—Standard, 0·75$\pm$0·05 w/v of morphine; S.G. 0·985 to 0·990; alcohol about 18 v/v. The morphine is determined as for *Tinct. Opii* (*q.v.* p. 271).

Other liquid extracts with their usual analytical characteristics are given in the following table. The figures are approximate except where definite limits are given.

	S.G.	Total Solid Extract, w/v.	Alcohol, v/v.
Ext. Belæ Liq., B.P. . . .	1·10	30	19
Ext. Cascaræ Sagradæ Liq., B.P.	1·06	23	23
Ext. Condurango Liq., B.P.C. .	0·960	10	51
Ext. Glycyrrhizæ Liq., B.P. .	1·13	40	18
Ext. Grindeliæ Liq., B.P. .	1·10	24	25
Ext. Hamamelidis Liq., B.P. .	1·03 to 1·05	18	32
Ext. Kavæ Liq., B.P. . .	0·861	6	80
Ext. Viburni Liq., B.P. . .	0·950	17	58

SECTION IV.

GLYCERINS.

Glycerinum Acidi Borici, B.P., contains 30 per cent. of boric acid. Boric acid may be determined by weighing out about 3 gm. in a weighing bottle, dissolving in 50 cc. of water, adding 20 cc. of glycerin, and titrating the mixture with *N*/2 sodium hydroxide, using thymol blue to a green colour. If the glycerin used is not neutral a blank must be subtracted for the amount added. 1 cc. *N*/2 NaOH ≡ 0·031 gm. boric acid.

Glycerinum Acidi Carbolici, B.P., contains 20 w/v of phenol, =16·3 per cent. Refractive index at 20° C., about 1·49.

Phenol.—Weigh out 1 gm. in a weighing bottle and dilute to 100 cc. with water in a graduated flask. Pipette 10 cc. of the solution into a stoppered bottle, add 5 cc. of hydrochloric acid and 15 cc. of *N*/10 bromide-bromate solution. Shake for one minute, not more, then add 5 cc. of potassium iodide solution, and titrate with *N*/10 thiosulphate using starch paste. 1 cc. *N*/10 bromide-bromate ≡ 0·001568 gm. phenol.

Glycerinum Acidi Tannici, B.P., contains 20 w/v of tannic acid. An approximate determination of tannic acid may be made by the following method: Weigh out 1 gm., dissolve in water, and add excess of copper acetate solution. Filter through a weighed Gooch crucible, wash, dry, and ignite to CuO. CuO × 1·45 = tannic acid.

Glycerinum Belladonnæ, B.P.C.—This preparation contains 50 w/v of *Ext. Bellad. Viride,* B.P. 1898. Alkaloids may be determined as under *Ext. Bellad. Liq.* (p. 241).

Glycerinum Boracis, B.P., contains 11·68 per cent. of borax. Refractive index at 20° C. about 1·4625.

Determination of Borax.—Weigh out 25 gm., dissolve in 100 cc. of water, and add 25 cc. of glycerin. Titrate with *N*/2 sodium hydroxide, using thymol blue to a green shade. 1 cc. *N*/2 NaOH ≡ 0·0955 gm. borax.

Glycerinum Pepsini, B.P., contains 10 w/v of pepsin, and 60 v/v of glycerin made acid with hydrochloric acid. The pepsin may be determined by the B.P. method (see p. 227), using 2·5 gm. of the preparation in place of 0·25 gm. pepsin.

Glycerinum Plumbi Subacetatis, B.P., contains lead subacetate equivalent to about 15·5 per cent. of lead. S.G. 1·48.

Lead.—Dilute 1 gm. with 20 cc. of water, and add an excess of saturated oxalic acid solution. Filter, wash and transfer the precipitate to a flask. Add an excess of dilute sulphuric acid, heat to 60° C., and titrate with *N*/10 permanganate until pink. 1 cc. *N*/10 $KMnO_4$ ≡ 0·01035 gm. Pb.

SECTION V.

LINIMENTS.

Linimentum Aconiti, B.P., is standardised to contain 0·2±0·01 w/v of ether-soluble alkaloids. S.G. about 0·868; total solids about 6 w/v; alcohol, about 77 v/v.

Determination of Ether-Soluble Alkaloids.—25 cc. of the liniment are evaporated to dryness with 10 gm. of sawdust at a temperature not exceeding 60° C., and the process continued as for Aconite Root (see p. 182).

Linimentum Aconiti Co., B.P.C. (*A. B. C. Liniment*).—S.G. about 1·015; total solids about 5·5 w/v; alcohol about 52 v/v.

Linimentum Belladonnæ, B.P., contains half its volume of *Ext. Bellad. Liq.*, B.P., and should therefore contain 0·375 w/v of belladonna alkaloids. S.G. about 0·925; total solids about 9 w/v; alcohol about 70 v/v. The alkaloidal content may be determined as for *Ext. Bellad. Liq.* (see p. 241), using twice the volume for the test.

Linimentum Camphoræ, B.P., contains 20 per cent. of camphor to 80 per cent. of olive oil. S.G. 0·920 to 0·925.

Camphor may be determined by heating about 2 gm. in a flat-bottomed dish on a water bath until the odour of camphor is no longer perceptible. After drying at 100° C. in an oven for half an hour the residue is weighed. The loss in weight represents camphor with sufficient accuracy for most purposes. Wallace and Plummer[1] determine the camphor by heating 5 gm. of liniment at 120° C. for five hours in the case of cotton-seed oil, and for four hours in the case of olive oil, allowing that 4 gm. of the oils gain 0·0142 gm. and 0·0138 gm. respectively when heated alone. Camphor may also be determined by observing the optical rotation, the calculated angular rotation for a 200 mm. tube being 0·98° to 0·99° for each per cent. of camphor. The possibility of the presence of synthetic camphor must of course be excluded. On the other hand, this method may be used in conjunction with the loss on heating method as a means of detecting the presence of synthetic camphor.[2]

The olive oil used in this preparation should be of B.P. quality. The U.S.P. uses cotton-seed oil instead of olive oil. Cheaper vegetable oils or mineral oils are sometimes used, and may be detected by the ordinary methods of oil analysis after removal of the camphor. It is stated that the presence of camphor does not materially affect the refractive index of olive oil.[3]

[1] *Amer. J. Pharm.*, 1921, 93, 600.
[2] See also Richardson and Walton, *Analyst*, 1908, 33, 463.
[3] *Analyst*, 1900, 25, 202.

Deficiency in strength in camphorated oil cannot be attributed to loss by volatilisation on storing provided that reasonable care is exercised.[1]

Linimentum Camphoræ Ammoniatum, B.P., contains 12·5 w/v of camphor. S.G. about 0·870; alcohol about 54 v/v.

Ammonia may be determined by titrating 5 cc. with $N/2$ hydrochloric acid to methyl red. The amount in the finished product is about 6·2 per cent.

Linimentum Opii, B.P., contains half its volume of tincture of opium, and hence contains 0·5 per cent. of morphine. S.G. about 0·935; total solids about 4·5 w/v; alcohol about 52 v/v. Morphine may be determined as under *Tinct. Opii* (p. 271).

Linimentum Saponis, B.P., contains camphor 4 w/v, and soft soap 8 w/v. S.G. about 0·890; total solid residue about 6 w/v; alcohol about 65 v/v.

Linimentum Sinapis, B.P., contains camphor, 5·5 w/v; mustard oil (essential), 3·5 w/v; castor oil, 12·5 w/v. S.G. about 0·870; alcohol about 65 v/v.

Castor Oil may be roughly determined as non-volatile residue remaining after heating in a thin layer on the water bath.

Allyl Isothiocyanate.—Dilute 30 cc. to 50 cc. with 90 per cent. alcohol. Take 5 cc. in a 100 cc. flask, and add 50 cc. of $N/10$ silver nitrate solution with 10 cc. of dilute ammonia solution. Keep in the dark for twenty-four hours, with occasional shaking, then place in a water bath at 80° C. for half an hour, shaking frequently. Cool, make up to the mark with water, and filter. Titrate 50 cc. of the filtrate with $N/10$ thiocyanate solution to ferric alum after adding 6 cc. of 25 per cent. nitric acid. The number of cc. of thiocyanate used is doubled and subtracted from 50. The result $\times 0{\cdot}33 =$ per cent. of allyl isothiocyanate in the liniment.

Linimentum Terebinthæ, B.P. (Liniment of Turpentine), contains 5 w/v of camphor and 65 v/v of oil of turpentine, emulsified with soft soap. The camphor and oil of turpentine may be determined together by distilling 50 gm. of the liniment with steam into a separator until no more oil comes over. The watery part of the distillate is separated from time to time and poured back into the boiler. The oil is separated and measured. It should amount to about 33 cc.

Linimentum Terebinthinæ Aceticum, B.P., contains 11 v/v of glacial acetic acid, 44·5 of v/v *Lin. Camphoræ*, and rectified oil of turpentine to 100 vols.

Camphor and Oil of Turpentine may be determined as under *Lin. Terebinth.*

Acetic Acid may be determined by titrating 2·5 gm. with $N/2$ sodium hydroxide to phenolphthalein, with the addition of alcohol. 1 cc. $N/2$ $NaOH \equiv 0{\cdot}03$ gm. of acetic acid.

Olive Oil may be determined by weighing the residue after the other constituents have been driven off on the water bath.

[1] Chapman, Dyer and Bevan, *Pharm. J.*, 1908, **25**, 68.

SECTION VI.

LIQUORES.

Liq. Acidi Chromici, B.P.—For determination and tests for purity, see Chromic Anhydride (p. 63). B.P. strength=25 w/v of chromic anhydride.

Liq. Ammoniæ, B.P. (see p. 40).

Liq. Ammonii Acetatis, B.P.—Solution of ammonium acetate, B.P., is prepared by adding sufficient ammonium carbonate to neutralise a definite amount of acetic acid. Since the means of testing neutrality in the B.P. is very indefinite, the B.P. preparation may vary considerably in pH value and in the amount of ammonia it contains. *Liq. Ammon. Acet.*, B.P., is often prepared by diluting the concentrated preparation *Liq. Ammon. Acet. Conc.*, which is eight times the strength of the B.P. preparation. The result, however, is not the same, since the B.P. solution is saturated with carbon dioxide, while the latter is not. The presence of the carbon dioxide renders necessary the addition of more ammonium carbonate than the equivalent of the acetic acid in order to make the solution neutral ($pH=7$).[1] *Liq. Ammon. Acet.* should be a colourless liquid, free from tarry odour. S.G. 1·016 to 1·018; pH value, 6·5 to 7·5. No appreciable residue should remain on evaporating 10 cc. to dryness and igniting. The solution should contain not more than traces of arsenic, heavy metals, chloride, or sulphates.

Determination of Ammonia.—Distil 10 cc. with excess of sodium hydroxide into 25 cc. of $N/2$ hydrochloric acid. Titrate the excess of hydrochloric acid with $N/2$ sodium hydroxide. 1 cc. $N/2$ HCl ≡ 0·0085 gm. ammonia. The B.P. preparation should contain 1·67 w/v NH_3.

Liq. Ammonii Acetatis Conc., 1 to 7, should be eight times the strength of the B.P. solution. S.G. 1·097 to 1·099; pH value for solution diluted eight times, about 7·0.

Ammonia.—Dilute 10 cc. to 100 cc. with water, and distil 20 cc. as under *Liq. Ammon. Acet.* From 13·0 to 13·5 per cent. should be present.

Liq. Ammonii Citratis, B.P., may be tested as given under *Liq. Ammon. Acet.* S.G. 1·057. For the determination of ammonia use 10 cc. [1 cc. $N/2$ HCl ≡ 0·04053 gm. $(NH_4)_3C_6H_5O_7$]. B.P. strength = 14·47 w/v $(NH_4)_3C_6H_5O_7$. The same considerations with regard to neutralisation apply in this case as with *Liq. Ammon. Acet.*

Liq. Arsenicalis, B.P. (Fowler's Solution).—A solution obtained by dissolving arsenious acid in a solution of potassium carbonate and flavouring with compound tincture of lavender.

Arsenious Oxide may be determined by taking 20 cc., making acid

[1] Allport and Cocking, *Pharm. J.*, 1927, **118**, 719.

with dilute hydrochloric acid, adding excess of sodium bicarbonate, and titrating with $N/10$ iodine solution, keeping an excess of sodium bicarbonate present throughout the titration. 1 cc. $N/10$ iodine ≡ 0·004948 gm. As_2O_3.

Potassium Carbonate may be determined by titrating 50 cc. with $N/2$ hydrochloric acid, using bromophenol blue as an indicator. (1 cc. $N/2$ HCl ≡ 0·03455 gm. K_2CO_3.) B.P. strength=1 w/v As_2O_3, and 1 w/v K_2CO_3. *Liq. Potassii Arsenitis*, U.S.P., is an identical preparation, except that it contains 2 per cent. of potassium bicarbonate instead of potassium carbonate.

Liq. Arsenici Hydrochloricus, B.P.—A solution of arsenious oxide in hydrochloric acid. Arsenious oxide may be determined as given under *Liq. Arsenicalis*. B.P. strength=1 w/v As_2O_3. Hydrochloric acid may be determined by titrating 20 cc. with $N/10$ sodium hydroxide to bromophenol blue. (1 cc. $N/10$ NaOH ≡ 0·003647 gm. HCl.) B.P. strength 0·38 w/v HCl.

Liq. Arsenii et Hydrargyri Iodidi, B.P. (Donovan's Solution).—A solution of arsenious iodide and red mercuric iodide in water. Arsenious iodide may be determined by taking 25 cc. of the solution, adding 25 cc. of water and 2 gm. of sodium bicarbonate, and titrating with $N/10$ iodine. (1 cc. $N/10$ iodine ≡ 0·02279 gm. AsI_3.)

Mercuric Iodide.—Take 25 cc., add 5 cc. of potassium hydroxide solution, and 5 cc. of formaldehyde solution, and warm until complete reduction has taken place. Wash the mercury carefully by decantation, dissolve it in 10 cc. of nitric acid and 50 cc. of water, add about 5 cc. of 2 per cent. potassium permanganate solution, or sufficient to keep the liquid pink for several minutes. Exactly decolorise with a weak solution of sodium nitrite, and titrate with $N/10$ ammonium thiocyanate. 1 cc. $N/10$ NH_4CNS ≡ 0·02272 gm. HgI_2. B.P. strength=1 w/v of each salt.

Liq. Atropinæ Sulphatis, B.P.—The atropine sulphate may be determined by making alkaline with ammonia and extracting with chloroform, or by the determination of the total solids. B.P. strength=1 w/v of atropine sulphate.

Liq. Bismuthi et Ammonii Citratis, B.P.—The solution should be colourless, slightly alkaline to litmus, and should have not more than the faintest odour of ammonia. pH value, 8·5 to 9·0.

Bismuth Oxide may be determined by evaporating 10 cc. to dryness and igniting with a few drops of nitric acid in a porcelain dish. The residue of bismuth oxide should be not less than 5 per cent.

Ammonia may be estimated by distillation.

Nitrate may be tested for by mixing 1 cc. with 5 cc. of conc. sulphuric acid in a test-tube, cooling, and carefully pouring 5 cc. of ferrous sulphate solution on the surface without mixing. No brown ring should be visible in the absence of nitrate. For quantitative determination the method given on p. 53 may be used after first distilling off all the ammonia.

Liq. Calcis, B.P. (Lime Water, Calcium Hydroxide Solution).—25 cc. are titrated with $N/10$ hydrochloric acid to phenolphthalein. 1 cc. $N/10$ acid ≡ 0·0028 gm. CaO. The B.P. requires that 10 cc. of the latter should be used, which corresponds to 0·112 w/v CaO. A saturated solution of lime in water at 15° C. actually contains 0·129 gm. of CaO in 100 cc. 50 cc. should give no coloration with 2 drops of sodium sulphide solution, showing absence of

lead. 50 cc. after acidifying with dilute nitric acid should give no opalescence with silver nitrate solution, showing absence of chlorides.

Liq. Calcis Chlorinatæ, B.P.—A solution of chlorinated lime in water.

Available Chlorine.—Pipette 5 cc. of the solution into 25 cc. of potassium iodide solution acidified with 5 cc. of dilute hydrochloric acid, and titrate the liberated iodine with $N/10$ thiosulphate solution. 1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·003546 gm. Cl_2. B.P. strength, not less than 2 per cent. (when freshly prepared, 3 per cent.).

Liq. Calcis Saccharatus.—Saccharated solution of lime is a solution of lime in sucrose solution. S.G. 1·055. It may be determined by titrating 20 cc. with $N/2$ HCl to phenolphthalein. 1 cc. $N/2$ HCl $\equiv$ 0·01852 gm. $Ca(OH)_2$. The solution should give no reaction for chlorides, reducing sugars, or lead. B.P. strength=2·44 w/v $Ca(OH)_2$.

Liq. Cresol Saponatus, B.P.—Compound solution of cresol (and similar preparations, lysol, etc.). *Liq. Cresol Saponatus* is a pale yellow to reddish-brown liquid, free from objectionable odour, readily miscible with water, forming a clear solution with distilled water. A 1 per cent. solution should not be alkaline to thymolphthalein solution. Free alkali and total alkali may be determined as given under Soap.

Cresols may be determined [1] by distilling 20 cc. with 40 cc. of glycerin and collecting 30 cc. of the distillate, not allowing the temperature to rise above 280° C. To the distillate 30 cc. of sulphuric acid (66 w/v) are added and the volume of cresols read off in a burette. *Liq. Cresol Saponatus*, lysol, and similar preparations should contain 50 w/v cresol. The cresols obtained in this way may be tested for purity by the usual methods.

Fatty Acids.—The residue in the flask is dissolved in 100 cc. of water, 20 cc. of N sulphuric acid are added, and the whole warmed till the fatty acids have separated, then transferred to a separator, cooled, washed out of the flask into the separator with a little ether, and the fatty acids extracted with 25 cc. of ether. The ether is distilled off and the acids dried and weighed.

Potassium.—10 gm. are mixed with 100 cc. of water, acidified with dilute hydrochloric acid, and the fatty acids removed with ether. The aqueous liquid is evaporated to dryness, and the residue gently ignited and weighed. In order to determine whether potassium or sodium or a mixture of both has been used in the preparation, the residue is dissolved in water, and titrated with $N/10$ silver nitrate. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·00746 gm. KCl or 0·00585 gm. NaCl.

β-Naphthol is sometimes used in cresol disinfectants in order to raise the Rideal-Walker coefficient. It may be detected by dissolving 1 cc. of the disinfectant in 100 cc. of water and adding 1 cc. of a solution containing 1 gm. of benzidine, 5 cc. of conc. hydrochloric acid, and 1 gm. of sodium nitrite in 100 cc. of water. A pure cresol preparation gives an orange colour, but in the presence of 0·2 per cent. of β-naphthol, a fine red colour is produced.[2] *Liq. Cresol Co.* is a similar preparation.

Liq. Ethyl Nitritis, B.P.—Solution of Ethyl Nitrite contains not less than 2·5 or more than 3 per cent. of ethyl nitrite dissolved in a mixture of alcohol and glycerin. S.G. 0·823 to 0·826; *p*H value not less than 2·0. No effervescence should occur when shaken with sodium bicarbonate

[1] Rapp, *Apoth. Ztg.*, 1909, **24**, 641.
[2] Bodmer, *Analyst*, 1915, **40**, 341.

solution, showing absence of free acid. 10 cc. mixed with 5 cc. of *N* NaOH and 5 cc. of water should not assume a yellow colour, showing absence of acetaldehyde.

Ethyl Nitrite may be determined as described under *Spt. Æther. Nitrosi* (p. 277). The B.P. requires 1 vol. to give at N.T.P. not less than 6·5 or more than 7·8 vols. of nitric oxide. (1 volume NO ≡ 0·38 per cent. ethyl nitrite.)

Alcohol is determined by the extraction process (see p. 265); content, about 9 v/v.

Liq. Ferri Dialysatus, B.P. 1885.—Dialysed Iron. A solution prepared by dissolving freshly precipitated ferric hydroxide in a solution of ferric chloride and dialysing. S.G. about 1·047.

Determination of Ferric Oxide.—Dialysed iron should contain about 5 per cent. of Fe_2O_3, which may be determined in the ordinary manner by precipitation as hydroxide.

Chloride.—Boil 5 cc. with 20 cc. of a 5 per cent. potassium hydroxide solution (free from chlorine) and 25 cc. of water. Filter, and wash with boiling water; cool the filtrate and make up to 100 cc. Mix 50 cc. of the filtrate (=2·5 cc. of dialysed iron) with 5 cc. of conc. nitric acid and 25 cc. of *N*/10 silver nitrate solution; heat on the water bath for thirty minutes, cool, and titrate the filtrate and washings with *N*/10 ammonium thiocyanate to ferric alum. 1 cc. *N*/10 $AgNO_3$ ≡ 0·003546 gm. Cl. For reagent purposes dialysed iron should be nearly free from chloride.

Liq. Ferri Perchloridi Fort., B.P. (Strong Solution of Ferric Chloride).—An orange-brown solution containing 20 w/v of iron. S.G. 1·45 (the B.P. is incorrect).

Arsenic.—Heat 1 cc. in a porcelain dish with 1 cc. of sulphuric acid until white fumes are evolved, cool, add an equal volume of water, and again heat till white fumes are evolved. Dissolve the residue in 10 cc. of water and 15 cc. of hydrochloric acid. Add stannous chloride solution drop by drop until the yellow colour disappears, and distil 20 cc. Add a few drops of bromine solution to the distillate and remove the excess by a few drops of stannous chloride solution. The determination is continued in the usual way. It should not show more than 10 parts of arsenic per million.

In the electrolytic method heat 1 cc. with sulphuric acid as above, and proceed as usual after adding 2 gm. of citric acid.

On adding a clear crystal of ferrous sulphate to a cooled mixture of equal volumes of sulphuric acid and of the strong solution diluted with nine times its volume of water, the crystal does not become brown nor does a brownish-black colour develop around it, showing absence of nitrates.

Iron.—Iron may be determined by diluting 10 cc. to 100 cc. with water in a graduated flask, taking 20 cc. of the solution, diluting to about 100 cc., precipitating with ammonia, and continuing as usual. The B.P. requires 28·4 w/v ferric oxide, ≡ 20 w/v iron.

U.S.P. Method.—Dilute 10 cc. to 100 cc., take 10 cc., add 5 cc. of hydrochloric acid, 25 cc. of distilled water, and about 3 gm. of potassium iodide. Stopper, and allow to stand thirty minutes at 40° C. Cool, dilute with 100 cc. of water, and titrate with *N*/10 thiosulphate. 1 cc. *N*/10 thiosulphate ≡ 0·005584 gm. Fe. Common impurities are lead, copper, zinc, calcium, sodium, potassium, ammonium, and ferrous salts.

Liq. Ferri Perchloridi, B.P. (Solution of Ferric Chloride).—B.P. strength= 5 w/v of iron. S.G. 1·072 to 1·115. It should answer to the tests and be free from the impurities given under *Liq. Ferri Perchlor. Fort.*

Determination.—Determine by using 5 cc. of undiluted solution as under *Liq. Ferri Perchlor. Fort.* *Liq. Ferri Chloridi,* U.S.P., contains 10 per cent. Fe.

Liq. Ferri Persulphatis, B.P.—S.G. about 1·441.

Arsenic may be determined by the method given under *Liq. Ferri Perchloridi Fort.*, using 2 gm. Limit, 5 parts per million.

Iron.—B.P. strength=2·08 w/v of ferric oxide. Determine by the method given under *Liq. Ferri Perchlor. Fort.*, using 10 cc. of undiluted solution. *Liq. Ferri Persulphatis,* U.S.P., contains 9·5 to 10·5 per cent. Fe.

Liq. Formaldehydi.—See p. 148.

Liq. Formaldehydi Saponatus, B.P.—Solution of formaldehyde with soap.

Constituents.—Soft soap, 40 w/v; alcohol (90 per cent.), 30 v/v; solution of formaldehyde, 20 v/v.

Formaldehyde may be determined by treating 10 gm. of the sample in a 100 cc. flask with a slight excess of barium chloride solution to precipitate the soap, and making up to 100 cc. After thorough mixing the liquid is filtered, and 5 cc. of the filtrate are treated with 50 cc. of *N*/10 iodine, then with sodium hydroxide solution drop by drop until the colour is discharged. After ten minutes the mixture is rendered acid with dilute sulphuric acid, and the liberated iodine titrated with *N*/10 thiosulphate. The number of cc. used subtracted from 50 and multiplied by 0·3 gives the equivalent of formaldehyde.

Alcohol content, 27 v/v.

Liq. Hamamelidis, B.P., is obtained by distilling fresh hamamelis leaves with dilute alcohol. S.G. about 0·982. The residue on evaporation should be practically nil. It contains about 14 v/v of absolute alcohol. As the essential oil is present in very small amount the alcohol may be calculated directly from the S.G. without serious error.

Liq. Hydrargyri Nitratis Acidus, B.P.—S.G. about 2·0.

Mercury may be determined in the usual way (p. 88). B.P. strength= 33·3 w/v Hg. No precipitate should be formed on diluting with water and adding hydrochloric acid, showing absence of mercurous salts. On evaporating to dryness and igniting, no appreciable residue should be obtained. It should be free from the impurities mentioned under Mercuric Nitrate.

Liq. Hydrargyri Perchloridi, B.P.—Mercury may be determined as sulphide. ($HgCl_2$=$HgS \times 1{\cdot}167$.) B.P. strength 0·1 w/v $HgCl_2$.

Liq. Hydrogenii Peroxidi, B.P.—See p. 73.

Liq. Magnesii Bicarbonatis, B.P. (Fluid Magnesia).—A clear, colourless solution, effervescing slightly or not at all when the container is opened.

Arsenic.—Treat 50 cc. with 13 cc. of brominated hydrochloric acid, remove the excess of bromine with a few drops of stannous chloride solution and proceed as usual. In the electrolytic method 50 cc. are treated by the method for carbonates. It should not contain more than 0·2 parts per million.

Lead.—Neutralise 100 cc. with a slight excess of acetic acid, evaporate to 60 cc., make alkaline with ammonia, and dilute to 75 cc. 50 cc. of this are used for the primary solution, the remaining 25 cc. being used as the

control with 5 cc. of dilute lead solution. It should not contain more than 0·5 part per million.

Determination.—Titrate 5 cc. with *N*/10 hydrochloric acid to methyl red. (1 cc. *N*/10 HCl ≡ 0·00201 gm. MgO.) Evaporate 20 cc. to dryness and ignite; a white residue should remain, weighing from 0·16 to 0·19 gm. ≡ 0·80 to 0·95 w/v MgO.

Sulphate.—25 cc. after acidifying with hydrochloric acid, should give no precipitate with 5 cc. of barium chloride solution, showing absence of sulphate.

Liq. Morphini Acetatis, B.P.—*Morphine* may be determined as described under *Liq. Morphin. Hydrochlor.* B.P. strength=1 w/v morphine acetate= about 0·71 w/v morphine.

Alcohol, 22·5 v/v; total solids, 0·86 w/v.

Liq. Morphini Hydrochloridi, B.P., is a solution in dilute alcohol of 1 w/v of morphine hydrochloride=0·76 w/v of morphine.

Morphine.—Dilute 0·4 cc. to 10 cc. Add 10 drops of *N* sulphuric acid and 10 drops of a cold, saturated solution of potassium iodate. Allow to stand five minutes, and add 10 drops of *Liq. Ammon. Fort.* After two minutes compare the colour with an equal amount of a standard 1 per cent. solution of morphine hydrochloride.

Alcohol, 22·5 per cent.; total solids, 0·86 w/v.

Liq. Morphini Tartratis, B.P.—Morphine may be determined as described under *Liq. Morphini Hydrochlor.* B.P. strength=1 w/v of morphine tartrate =0·73 to 0·745 w/v of morphine.

Alcohol, 22·5 v/v.

Liq. Pancreatis, B.P.—The B.P. gives the following test for proteolytic properties: 3 cc. of the solution with 0·2 gm. of sodium bicarbonate and 20 cc. of water are added to 80 cc. of milk, and kept at 45° C. for one hour. On placing 5 cc. of the liquid with 5 cc. of ether and 5 drops of nitric acid in a stoppered tube and mixing by gently inverting three times, no curdy precipitate occurs in the lower layer. See also Pancreatin (p. 226).

Liq. Plumbi Subacetatis Fortis, B.P. (Strong Solution of Lead Subacetate).—A clear, colourless solution, alkaline to litmus. S.G. 1·275.

Lead.—Dilute 1 gm. with 20 cc. of water, and mix with excess of oxalic acid solution. Collect the precipitate, wash, transfer to a flask, and decompose with dilute sulphuric acid. Heat the liquid to 60° C., and titrate with *N*/10 $KMnO_4$. (1 cc. N/10 $KMnO_4$ ≡ 0·1035 gm. Pb.) The B.P. requires not less than 17 cc. of *N*/10 $KMnO_4$ to be used ≡ 17·6 per cent. Pb. *Liq. Plumbi Subacetatis Dilutus,* B.P., is one-eighth of the strength of the strong solution, w/v.

Liq. Potassæ, B.P.—A solution of 5 w/v of potassium hydroxide in water. S.G. 1·045. It may be determined by titrating 20 cc. with *N*/2 HCl. to phenolphthalein. (1 cc. *N*/2 HCl ≡ 0·02805 gm. KOH.) See also Potassium Hydroxide (p. 95).

Liq. Potassii Permanganatis, B.P., contains 1 per cent. potassium permanganate.

Determination.—Pipette 10 cc. into 25 cc. of potassium iodide solution and titrate the liberated iodine with 25 cc. of *N*/10 thiosulphate (1 cc. *N*/10 $Na_2S_2O_3$ ≡ 0·003161 gm. $KMnO_4$). See also Potassium Permanganate (p. 98).

Liq. Sodæ Chlorinatæ, B.P. (Solution of Chlorinated Soda).—S.G. 1·054.

Not more than traces of calcium or carbonates should be present. Available chlorine may be determined by pipetting 5 cc. into 25 cc. of potassium iodide solution, and titrating the liberated iodine with $N/10$ thiosulphate (1 cc. $N/10$ $Na_2S_2O_3 \equiv 0{\cdot}003546$ gm. available chlorine). The B.P. and U.S.P. require not less than 2·5 w/v of available chlorine.

Liq. Sodæ Chlorinatæ Chirurgicalis, U.S.P.—Modified Dakin's Solution is a solution of sodium hypochlorite stabilised with sodium phosphate and containing from 0·43 to 0·48 per cent. of available chlorine. The original Dakin's solution was stabilised with boric acid and contained 5 per cent. of available chlorine.

Liq. Sodii Arsenatis.—See Sodium Arsenate (p. 102). B.P. strength 1 w/v of sodium arsenate.

Liq. Strychninæ Hydrochloridi, B.P., contains 1 w/v of strychnine hydrochloride. The strychnine hydrochloride may be determined from the total solids, or by making alkaline with ammonia and extracting the strychnine with chloroform. Alcohol, 22·5 v/v.

Liq. Trinitrini, B.P., is a solution of 1 gm. of trinitroglycerin in 100 cc. of 90 per cent. alcohol. S.G. 0·840. B.P. test for a due amount of trinitroglycerin: 10 cc. with 10 cc. of water is clear at 15·5° C., but the addition of a further 1 cc. of water causes opacity. On further diluting with water and setting aside the mixture, there is deposited a liquid of oily consistency, one drop of which, absorbed by paper and struck with a hammer on a hard surface, explodes. See also Nitroglycerin (p. 159).

Liq. Zinci Chloridi.—S.G. 1·530. It may be determined by weighing about 0·4 gm., diluting with 50 cc. of water, and titrating with $N/10$ $AgNO_3$ as for chlorides. (1 cc. $N/10$ $AgNO_3 \equiv 0{\cdot}006815$ gm. $ZnCl_2$.) B.P. strength=83·4 w/v $SnCl_2$ or 54·5 per cent. The U.S.P. *Liq. Zinci Chloridi* contains 48·5 to 52 per cent. $ZnCl_2$. Common impurities are copper, cadmium, iron, calcium, magnesium, and sulphates.

Arsenic.—10 cc. by general method or electrolytically by method for Chlorides (see p. 33).

SECTION VII.

OINTMENTS.

In the examination of ointments the chief difficulty is the satisfactory separation of the active ingredient from the fatty material which forms the base. If necessary the base itself may be examined by the methods used in the examination of fatty oils. The refractive index provides a useful indication of whether the right base has been used,[1] but the active constituent itself in some cases causes a considerable shift in the refractive index.

Ung. Acidi Borici, B.P.—Boric acid ointment contains 10 per cent. of boric acid. Weigh 3·1 gm. of the sample into a 150 cc. wide-mouthed flask and add 50 cc. of water. Boil the liquid for a few minutes after making acid to methyl orange with hydrochloric acid, and allow to cool. Neutralise to methyl orange with $N/2$ caustic soda, and add 25 cc. of neutral glycerin. Complete the titration with $N/2$ sodium hydroxide to phenolphthalein. Each cc. of $N/2$ caustic soda used, after the addition of glycerin, is equivalent to 1 per cent. of boric acid. It is not satisfactory to calculate the ash as B_2O_3 unless the heating is done very carefully.[2] This method may, however, be used for confirmation.

Ung. Acidi Carbolici, B.P. (Phenol Ointment).—Carbolic acid ointment is made with 3 per cent. of phenol in paraffin ointment base. Owing to loss in manufacture the finished ointment contains about 2·5 per cent. of phenol.

Determination of Phenol.—Weigh 0·5 to 0·6 gm. of the ointment into a 150 cc. wide-mouthed flask and dissolve by gently warming in 5 cc. of chloroform. Add 25 cc. of $N/10$ sodium carbonate, and heat the flask over a small flame with constant shaking until the liquid is boiling freely. The shaking being continued, add 25 cc. of cold water and cool under the tap. Add 15 cc. of $N/10$ iodine, shake the liquid thoroughly, and allow to stand for five minutes (no longer). Add 15 cc. of $N/10$ sulphuric acid, and titrate the excess of iodine with $N/10$ thiosulphate solution. Care must be taken that the chloroform has practically no colour at the end of the titration. 1 cc. $N/10$ iodine $\equiv$ 0·001568 gm. phenol.

Refractive index (60° *C.*), 1·450 to 1·456. *Ung. Phenolis,* U.S.P., contains 2 per cent. phenol.

Ung. Acidi Salicylici, B.P.—Salicylic acid ointment is made with 2 per cent. salicylic acid in paraffin ointment. Slight loss may occur during manufacture.

Determination of Salicylic Acid.—1·0 to 1·2 gm. of the ointment are

[1] Evers and Elsdon, *Analyst*, 1922, **47**, 197.
[2] Cf. *Analyst*, 1918, **43**, 138.

treated as given under *Ung. Acidi Carbolici.* 1 cc. N/10 iodine ≡ 0·002301 gm. salicylic acid.

Refractive index (60° C.), 1·445 to 1·450.

Ung. Atropinæ, B.P.—Atropine ointment contains 2 per cent. of atropine.

Determination of Atropine.[1]—Weigh 2 gm. of the ointment into a 50 cc. beaker and dissolve in 10 cc. of chloroform. When solution is complete, transfer to a separator, add 20 cc. of N/20 sulphuric acid, shake the whole well, and allow to separate. Separate the acid solution and wash the chloroform layer twice with 10 cc. of water, the water being added to the acid liquid. Titrate the acid liquid with N/20 potassium hydroxide to bromophenol blue. 1 cc. N/10 H_2SO_4 ≡ 0·01446 gm. atropine ($C_{17}H_{23}NO_3$).

Refractive index (60° C.), 1·450 to 1·451.

Ung. Cantharidini, B.P.—Cantharidin ointment contains 0·033 per cent. of cantharidin.

Determination of Cantharidin.—Dissolve 20 to 30 gm. in a mixture of equal parts of ether and chloroform, transfer to a separator, and wash three times with 15 cc. of a 5 per cent. solution of sodium carbonate. Filter the mixed alkaline washings, transfer to a separator, acidify with sulphuric acid, and extract three times with chloroform (about 10 cc. each time). Evaporate the mixed chloroformic washings to dryness. Wash the residue with two or three small quantities of a mixture of equal parts of petroleum ether and dehydrated alcohol saturated with cantharidin, and filter the washings through a plug of cotton-wool placed in a funnel and treated with chloroform and the petroleum ether-alcohol mixture. Dissolve the cantharidin in the dish in chloroform (2 or 3 small quantities), pour through the cotton-wool, and collect in a tared dish. Evaporate the chloroformic extract, dry the residue in the desiccator, and weigh as cantharidin.

Ung. Cetacei, B.P.—Spermaceti ointment contains spermaceti, 20 per cent.; white beeswax, 8 per cent.; liquid paraffin, 72 per cent., and should have analytical figures in agreement with this composition. Iodine value, not more than 3·0. Saponification value about 25.

Refractive index (40° C.), 1·461 to 1·463.

Ung. Chaulmoogræ, B.P.—Chaulmoogra ointment contains 10 per cent. of chaulmoogra oil with 40 per cent. of hard and 50 per cent of soft paraffin.

Refractive index (60° C.) 1·447 to 1·451. The saponification value should be about 20 and the iodine value about 11. Optical rotation for a 10 per cent. solution in chloroform, about +0·5°.

Ung. Chrysarobini, B.P.—Chrysarobin ointment contains 4 per cent. of chrysarobin in a soft paraffin base.

Refractive index (60° C.), 1·467 to 1·474. The U.S.P. ointment contains 6 per cent. of chrysarobin in hydrous wool fat.

Ung. Cocainæ, B.P.—Cocaine ointment contains 4 per cent. of cocaine.

Determination of Cocaine.—2 gm. of the ointment are treated as under Atropine Ointment.[1] 1 cc. N/20 H_2SO_4 ≡ 0·01516 gm. cocaine ($C_{17}H_{21}NO_4$).

Refractive index (60° C.), 1·450 to 1·454.

Ung. Creosoti, B.P.—Creosote ointment is made with 10 per cent. of creosote, but may lose a part of this by volatilisation during manufacture.

Determination of Creosote.—Weigh out 1 gm. into a flat-bottomed metal dish and heat on the water bath until there is no odour of creosote and no further loss in weight. The total loss in weight may be taken as creosote.

[1] Foster, *Y.B.P.*, 1921, 363.

Refractive index (60° C.), 1·453 to 1·457.

Ung. Eucalypti, B.P.—Eucalyptus ointment is made with 10 per cent. of eucalyptus oil. Some of this may be lost during manufacture.

Determination of Eucalyptus Oil.—This may be determined in the same way as creosote in creosote ointment.

Refractive index (60° C.), 1·445 to 1·451.

Ung. Gallæ, B.P.—Gall ointment is made with 20 per cent. of powdered galls. The percentage of galls may be determined by extracting from 2 to 5 gm. in a fat-free thimble in a Soxhlet apparatus with light petroleum, the thimble having previously been dried and weighed. The weight of residue so obtained can be taken for most purposes as the weight of the original galls, as galls are not appreciably soluble in petroleum ether. The residue should be examined microscopically and the matter soluble in alcohol (about 70 per cent.) may be determined if desired.

Refractive index (60° C.), 1·451 to 1·458.

Ung. Gallæ cum Opio, B.P. (Gall and Opium Ointment).—The total percentage of galls and opium may be determined as given under Gall Ointment. The residue should be examined microscopically and should be tested for morphine. B.P. strength, 92·5 per cent. gall ointment and 7·5 per cent. opium. Total residue insoluble in petroleum ether should be about 26 per cent.

Ung. Hydrargyri, B.P.—Mercury ointment contains 30 per cent. of mercury in a base of lard and suet.

Determination of Mercury.—Heat 3 gm. of the ointment in a 100 cc. extraction flask on the water bath with 20 cc. of conc. nitric acid until the mercury is dissolved and the evolution of fumes ceases. Dilute the mixture with about an equal quantity of water and warm until the fat has risen to the surface. Cool, and decant the liquid from the cake of fat, which is subsequently broken up, washed twice with water, and the washings added to the original liquid. Dilute the bulked liquids to about 75 cc. and completely oxidise by the gradual addition of potassium permanganate solution, excess of the latter being removed by means of a dilute solution of ferrous sulphate. The whole is then diluted to 100 cc., filtered, and the mercury determined in the filtrate by titrating 25 cc. with *N*/10 thiocyanate in the usual way.[1] 1 cc. of *N*/10 thiocyanate ≡ 0·0100 gm. Hg. *Ung. Hydrarg. Fortius*, U.S.P., contains 49 to 51 per cent. of mercury. *Ung. Hydrargyri Mite*, U.S.P., contains 29 to 31 per cent. of mercury.

Ung. Hydrargyri Ammoniati, B.P. (White Precipitate Ointment).—Ammoniated mercury ointment contains 5 per cent. of ammoniated mercury in a lard basis.

Determination of Ammoniated Mercury.—Treat 5 gm. with 25 cc. of dilute hydrochloric acid (S.G. 1·03), and wash as described under *Ung. Hydrarg.* Transfer 25 cc. of the final filtrate to a stoppered flask and add 0·5 to 1·0 gm. of potassium iodide, 20 cc. of 10 per cent. solution of caustic potash, 10 cc. of water, and finally 3 cc. of formaldehyde solution. Acidify with acetic acid, add 20 cc. of *N*/10 iodine solution, and shake until all the reduced mercury is dissolved. Titrate the unused iodine with *N*/10 thiosulphate. 1 cc. *N*/10 iodine ≡ 0·0126 gm. ammoniated mercury.[1] For an alternative method, see Elsdon.[2] *Ung. Hydrarg. Ammon.*, U.S.P., contains 10 per cent. of ammoniated mercury.

[1] Rupp, *Y.B.P.*, 1907, 103.

[2] *Y.B.P.*, 1911, 477.

Ung. Hydrargyri Co., B.P.—Compound mercury ointment contains 40 per cent. of mercury ointment with camphor, olive oil, and yellow beeswax.

Mercury may be determined as given under Mercury Ointment. B.P. strength, 12 per cent. of mercury.

Camphor should be determined by heating about 2 gm. contained in a flat-bottomed dish on the water bath for two hours; the loss is due to camphor. B.P. strength, 12 per cent. of camphor.

Ung. Hydrargyri Iodidi Rubri, B.P.—Mercuric iodide ointment (red) contains 4 per cent. red mercuric iodide in a lard basis. The solution of the mercuric iodide may be carried out by a method similar to that used for mercury ointment, using 10 per cent. potassium iodide solution in place of nitric acid. The mercuric iodide may be determined volumetrically by the method given under *Ung. Hydrarg. Ammon.* (1 cc. $N/10$ iodine ≡ 0·02272 gm. HgO).

Ung. Hydrargyri Nitratis, B.P.—Mercuric nitrate ointment contains about 6·5 per cent. of mercury. The mercuric nitrate may be removed as given under Mercury Ointment, using dilute nitric acid (S.G. 1·04), and the mercury may be determined in the same way. The diluted ointment (*Ung. Hydrarg. Nitrat. Dil.*, B.P.) is one-fifth of the strength and may be examined in the same way, using a proportionally larger amount.

Ung. Hydrargyri Oleatis, B.P.—Mercuric oleate ointment contains 25 per cent. of oleated mercury in a lard basis.

Determination of Mercury.—Heat 5 gm. of the ointment in a Kjeldahl flask with about 35 to 40 cc. of a mixture of concentrated nitric acid and sulphuric acid (approx. 2 : 1) until colourless or nearly so; then, whilst warm, add sufficient water to keep the mercuric sulphate in solution, and, if necessary, boil the solution. Cool, and add sufficient potassium permanganate to make the liquid distinctly red. Decolorise with ferrous sulphate solution, dilute to 200 cc., and titrate 100 cc. with $N/10$ ammonium thiocyanate, using 5 cc. of iron alum indicator (1 cc. $N/10$ NH_4CNS ≡ 0·01083 gm. HgO). B.P. standard, 5 per cent. HgO.

Ung. Hydrargyri Oxidi Flavi, B.P.—Yellow mercuric oxide ointment contains 2 per cent. of yellow mercuric oxide in a soft paraffin base.

Mercury may be determined by the method given under *Ung. Hydrarg.*, using nitric acid, S.G. 1·04, and about 10 gm. of the ointment (1 cc. $N/10$ NH_4CNS ≡ 0·0108 gm. HgO). *Ung. Hydrargyri Oxidi Flavi,* U.S.P., contains 1 per cent. of yellow mercuric oxide.

Ung. Hydrargyri Oxidi Rubri, B.P.—Red mercuric oxide ointment contains 10 per cent. of red mercuric oxide in paraffin ointment.

Mercury is determined as above, using 2 gm.

Ung. Hydrargyri Subchlor., B.P.—Calomel ointment contains 20 per cent. of mercurous chloride in a lard base.

Determination of Calomel.—Dissolve 5 gm. in ether, filter through paper, wash the paper with ether and dry. Drop the residue with the paper into a stoppered bottle, add 50 cc. of potassium iodide solution (10 per cent.) and 50 cc. of $N/10$ iodine solution. After complete solution has taken place titrate the excess of iodine with $N/10$ thiosulphate (1 cc. $N/10$ iodine ≡ 0·0236 gm. HgCl).

Refractive index (60° *C.*), 1·451 to 1·458.

Ung. Iodi, B.P.—Iodine ointment is made with 4 per cent. each of iodine and potassium iodide.

Iodine.—Dissolve 5 gm. of the ointment in chloroform, add water, and titrate the free iodine with $N/10$ thiosulphate. (1 cc. $N/10$ $Na_2S_2O_3 \equiv$ 0·01269 gm. I). The free iodine present is usually about 70 per cent. of that actually added.[1]

Potassium Iodide.—Wash out the melted ointment with water in a similar manner to the process given under Mercury Ointment. After boiling to remove any free iodine, titrate the potassium iodide with $N/10$ silver nitrate solution (1 cc. $N/10$ $AgNO_3 \equiv$ 0·01660 gm. KI). The U.S.P. ointment is of the same strength.

Ung. Iodi Denigrescens, B.P.C. (Non-staining Iodine Ointment).—This ointment is prepared with 5 per cent. of iodine, which is practically all absorbed by the base during the manufacture. It should not have any odour of free iodine and should not stain the skin brown. It should not contain more than 0·5 per cent. of free iodine, as determined by shaking out 2·5 gm. with three quantities of warm potassium iodide solution, and titrating the solution with $N/10$ thiosulphate.

Ung. Iodoformi, B.P.—Iodoform ointment contains 10 per cent. of iodoform.

Iodoform.—Heat 5 gm. of the ointment under a reflux condenser with 50 cc. of $N/10$ silver nitrate solution for two hours. Cool, dilute to 110 cc., boil, cool, and filter. Titrate 100 cc. of the filtrate with thiocyanate solution in the usual way (1 cc. $N/10$ $AgNO_3 \equiv$ 0·01312 gm. CHI_3). The result may be checked by the method given under Creosote Ointment.

Refractive index (60° *C.*) 1·451 to 1·458.

Ung. Myrobalani, B.P., and **Ung. Myrobalani cum Opio,** B.P. (Myrobalan Ointment and Myrobalan and Opium Ointment).—These may be examined by the methods given under Gall Ointment and Gall and Opium Ointment. The B.P. strengths are the same as for these, myrobalans being substituted for galls.

Ung. Paraffini, B.P.—Paraffin ointment is made with 27 per cent. of hard paraffin, 70 per cent. of soft paraffin (white or yellow), and 3 per cent. of white beeswax.

Refractive index (60° *C.*):—If made with white, soft paraffin the figure usually lies between 1·448 and 1·454, and if made with yellow, soft paraffin, between 1·458 and 1·463.

Ung. Picis Liquidæ, B.P.—Tar ointment contains 70 per cent. of tar with 25 per cent. of yellow beeswax and 5 per cent. of lard. When heated in a flat-bottomed metal dish on the water bath for about twenty hours, 1 gm. loses about 20 per cent. of its weight.

Refractive index (60° *C.*), 1·485 to 1·504.

Ung. Plumbi Iodidi, B.P. (Lead Iodide Ointment).—This may be examined as given under Gall Ointment, the lead iodide being isolated and weighed. B.P. strength, 10 per cent. of lead iodide.

Ung. Plumbi Subacet., B.P.—Lead subacetate ointment contains 12·5 per cent. of *Liq. Plumbi Subacet. Ft.*, in a paraffin base.

Determination.—The ointment may be extracted by boiling dilute acetic acid as given under Mercury Ointment and the lead determined in the usual way. B.P. strength, not less than 2·2 per cent. of lead.

Ung. Potassii Iodidi, B.P.—Potassium iodide ointment contains 10 per cent. of potassium iodide and 0·6 per cent. of potassium carbonate in a lard

[1] *Y.B.P.*, 1913, 355; 1915, 270; 1917, 103; 1918, 334.

base. The potassium iodide may be washed out with boiling water as given under *Ung. Hydrargyri*, and determined in the usual way after neutralisation to phenolphthalein. (1 cc. $N/10$ $AgNO_3 \equiv 0{\cdot}0166$ gm. KI).

Ung. Resinæ, B.P.—Resin ointment consists of resin, 26 per cent.; yellow beeswax, 26 per cent.; olive oil, 26 per cent.; lard, 22 per cent. The acid values of these constituents are :—

	Range.	Average.
Resin . . .	150 to 185	167
Beeswax . .	16·8 to 22·4	19·6
Olive oil . .	1 to 6	3
Lard . . .	0 to 1·2	..

From these figures calculation shows that the range of possible acid values for *Ung. Resinæ* is 43·4 to 55·2, and the average figure will be 49·3. Allowing average values for the constituents, the approximate percentage of resin may be calculated from the formula $\frac{(a-5{\cdot}9)\times 100}{167}$, where a is the acid value found.

Refractive index (60° C.), 1·460 to 1·470.

Ung. Sulphuris, B.P.—Sulphur ointment contains 10 per cent. of sublimed sulphur in a lard basis.

Sulphur may be determined by extraction with petroleum ether and weighing the residue as given under *Ung. Gallæ*, or as follows: Heat 0·5 gm. over a small flame with 5 cc. of conc. nitric acid and 3 cc. of bromine. When the excess of bromine is removed dilute with water and transfer to a separator. Extract the fat with three quantities of ether, and wash the mixed ethereal solutions twice with 5 cc. of water, adding the washings to the aqueous liquid. Add barium chloride solution and determine sulphate in the usual way. ($S = BaSO_4 \times 0{\cdot}1374$.)

Ung. Zinci, B.P.—Zinc ointment contains 15 per cent. of zinc oxide in a benzoated lard basis. The zinc oxide may be determined by igniting about 2 gm. very carefully and weighing the ash, or as follows: Weigh out about 2 gm. into a small funnel having the stem broken off, place in a separator in the oven until melted. Wash the ointment remaining in the funnel into the separator with 20 cc. of hot dilute hydrochloric acid, followed by 10 cc. of warm petrol (B.P. about 100° C.), and a further 10 cc. of the acid. Wash the fat with a further 20 cc. of hot acid. Cool the mixed acid extracts, filter, and wash the filter paper. Make slightly alkaline with ammonia, and warm to 80° C. Add ammonium sulphide solution until the zinc is completely precipitated, and warm on the water bath until the precipitate settles. Filter, wash with water containing a few drops of ammonium sulphide solution, dissolve the precipitate in dilute nitric acid, evaporate to dryness, ignite, and weigh as ZnO.

Ung. Zinci Oxidi, U.S.P., contains 20 per cent. of zinc oxide in a paraffin and petrolatum base.

SECTION VIII.

SYRUPS.

Syrupus, B.P.—Simple syrup should be clear and colourless and should have the following characteristics: S.G. 1·330; optical rotation, +56° to +58°.

Syrupus Acidi Hydriodici, B.P.—Syrup of hydriodic acid contains 10 w/v of diluted hydriodic acid, B.P. S.G. about 1·3.

Determination of Hydriodic Acid.—Dilute 25 cc. to 100 cc. with water, add 5 cc. of dilute nitric acid, and run in 25 cc. of *N*/10 silver nitrate solution from a pipette. Add 2 cc. of ferric ammonium sulphate solution, and titrate back with *N*/10 thiocyanate until a red colour appears. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·01279 gm. HI. B.P. strength, 1 w/v HI.

Syrupus Calcii Lactophosphatis, B.P.—Syrup of calcium lactophosphate contains about 0·95 w/v calcium and about 3 w/v phosphoric acid.

Phosphoric Acid may be determined by precipitation with ammonium molybdate, redissolving the precipitate, and reprecipitating as magnesium ammonium phosphate in the usual manner.

Calcium may be determined by precipitation as oxalate from the filtrate from the ammonium phosphomolybdate after making alkaline with ammonia.

Syrupus Codeinæ Phosphatis, B.P.—Syrup of codeine phosphate contains 0·5 w/v codeine phosphate, equivalent to 0·345 w/v codeine (anhydrous). S.G. 1·32.

Determination of Codeine.—20 cc. of the syrup are diluted with 50 cc. of water, made alkaline with ammonia, and extracted four times with 10 cc. of chloroform; the chloroform is distilled off and the codeine dried at 100° C. and weighed.

Syrupus Ferri Iodidi, B.P.—Syrup of ferrous iodide contains about 7 w/v of ferrous iodide or 4·9 to 5·1 per cent.

Ferrous Iodide Determination.—5 gm. are diluted with 50 cc. of water, 5 cc. of dilute nitric acid added, and 20 cc. of *N*/10 silver nitrate pipetted in. 2 cc. of ferric ammonium sulphate solution are added, and the solution titrated back with *N*/10 thiocyanate until a pink colour appears. 1 cc. *N*/10 $AgNO_3 \equiv$ 0·01548 gm. FeI_2.

Kolthoff[1] suggests the following method of titrating ferrous iron and iodide in the same sample. Weigh out about 3 gm. of the syrup, add a mixture of 10 cc. of 25 per cent. phosphoric acid (free from phosphorous acid), 5 cc. of 10 per cent. potassium cyanide solution, and 85 cc. of water. Titrate with *N*/10 permanganate until a faint rose colour appears (=*a* cc.). Add 5 cc. *N* potassium iodide solution, and titrate the liberated iodine

[1] *Pharm. Weekblad*, 1925, 62, 910.

with $N/10$ thiosulphate to starch ($=b$ cc.). Iodine content$=b\times\frac{12\cdot69}{2}$ mgm., and ferrous iron content$=(a-b)\times5\cdot58$ mgm.

Syrupus Ferri Phosphatis, B.P. *Determination of Iron.*—See *Syr. Ferri Phosph. Co.* below. B.P. strength, 0·86 w/v Fe.

Syrupus Ferri Phosphatis Co., B.P.C. (Parrish's Food; Chemical Food).—S.G. 1·31 to 1·32.

Total Iron.[1]—Measure 5 or 10 cc. into a 100 cc. flask, add a few drops of hydrochloric acid, and run in $N/10$ permanganate solution until a transitory purple is produced throughout the solution. The purple colour vanishes rapidly, and the iron present is entirely in the ferric state. Add an equal bulk of strong hydrochloric acid and a little sodium bicarbonate to give an atmosphere of carbon dioxide in the flask; add 1 drop of $N/10$ titanous chloride solution and mix a drop of the resulting solution with a drop of freshly prepared ferricyanide solution on a white tile; a blue coloration generally results, except in cases where a great excess of permanganate has been added, and in these cases titanous chloride must be added till a reaction for ferrous iron is given. Titrate the solution, which has the usual bright yellow colour of ferric salts in strong hydrochloric acid, add an excess of ammonium thiocyanate solution, and continue the titration until the red colour just disappears. 1 cc. $N/10$ $TiCl_3\equiv0\cdot0056$ gm. Fe.

The colorimetric method given under Easton's Syrup below may also be used, taking 10 cc. of the syrup instead of 5 cc., in which case 1 cc. standard iron solution ≡ 0·08 w/v Fe. The theoretical amount of total iron according to the B.P.C. formula is 0·437 per cent.

Ferric Iron may also be determined as under Easton's Syrup. The slight tinge of cochineal which remains after dilution may be allowed for by matching against standard iron solution and thiocyanate (the colour is of the same tint as ferric thiocyanate), and subtracting the amount required from the final result.

Syrupus Ferri Phosphatis cum Quinina et Strychnina, B.P. (Easton's Syrup).—S.G. about 1·27.

Total Iron.—See *Syr. Ferri Phosph. Co.* above.

Colorimetric Method.[2]—Boil 5 cc. for about a minute with 5 cc. of strong nitric acid and 50 cc. of water. After cooling the solution, dilute to 100 cc. and then take 5 cc. for comparison in a Nessler cylinder. After diluting to about 30 cc., add 5 cc. of dilute hydrochloric acid and 5 cc. of 10 per cent. potassium thiocyanate solution. Mix immediately and dilute to 50 cc. Match the colour immediately against a standard prepared from dilute ferric chloride solution (1 cc. ≡ 0·00002 gm. Fe) and the same volumes of reagents. When the final comparison of colours is made, the thiocyanate should be added to the solution of the iron and not *vice versa*. The colours should be compared immediately, as they fade after about ten minutes. 1 cc. of standard iron solution ≡ 0·16 w/v Fe. B.P. strength, 0·86 w/v Fe.

Ferric Iron.—Dilute 10 cc. to 100 cc. with air-free water, 10 cc. of this again to 100 cc., and take 20 cc. for comparison. Determine the iron as before. 1 cc. standard iron solution ≡ 0·01 w/v ferric iron.

[1] Droop Richmond, and Ison, *Analyst*, 1920, **45**, 259.
[2] Evers, *Analyst*, 1915, **40**, 447.

Total Alkaloids.—Pipette 50 cc. into a separator, add 2 gm. of citric acid and 50 cc. of water. When the citric acid has dissolved, make alkaline with ammonia. Extract the alkaloids by shaking with ether-chloroform (1 : 2) a number of times until a few drops of the aqueous liquid after acidifying give no precipitate with Mayer's reagent. Wash the mixed ether-chloroform extracts by shaking with 25 cc. of water. Evaporate the solvent, dry the residue at 110° C., and weigh. After subtracting the strychnine, the remainder is anhydrous quinine. Quinine (anhydrous) × 1·36=quinine sulphate (B.P.). The B.P. strength is 1·48 w/v of quinine sulphate.

Strychnine.[1]—Dissolve the total alkaloids in 10 cc. of dilute sulphuric acid and 50 cc. of water. Almost neutralise with ammonia until the precipitated quinine only just redissolves. Add 30 gm. of Rochelle salt, and neutralise the liquid with dilute ammonia, leaving faintly acid to litmus paper. Stir, and heat on a water bath for fifteen minutes, cool, and transfer to a 100 cc. measuring flask, the beaker being rinsed with water so as to make the volume up to 100 cc. After standing two hours, filter, the first 10 cc. being rejected. After making alkaline with ammonia, extract 50 cc. of the filtrate three times with chloroform, using 30 cc., 10 cc., and 10 cc., the mixed chloroform solutions being washed twice with 5 cc. of water. Extract the chloroform with 30 cc. of 10 w/v sulphuric acid and twice more with 10 cc. of the same acid, the acid liquids being collected in a small (60 cc.) separator previously plugged with a small piece of cotton-wool. Add 5 cc. of freshly made 4 per cent. potassium ferrocyanide solution, and nearly fill the separator with 10 per cent. sulphuric acid (to exclude air), and after rotation allow to stand in a dark place for two hours. It is advisable to be sure that precipitation has definitely occurred before placing aside. At the end of this time force out the acid through a plug, wash the strychnine ferrocyanide twice with 3 cc. of 5 per cent. sulphuric acid, and recover the strychnine by shaking with 10 cc. of 10 per cent. ammonia and 15, 10, and 10 cc. of chloroform. Evaporate as usual, an addition of about three drops of amyl alcohol being made towards the end to prevent decrepitation of the strychnine crystals. When cold, wash the alkaloidal residue three times with 1 cc. of ether and dry at 100° C. A correction of −1·7 per cent. is made for the volume of the quinine tartrate. B.P. strength, 0·057 w/v.

The following method [2] is simpler and gives reasonably satisfactory results. Shake 50 cc. of the syrup with 50 cc. of $4N$ hydrochloric acid and 50 cc. of chloroform continuously for five minutes. Separate carefully, taking care that no aqueous liquid passes into the flask with the chloroform. Extract with four further quantities of 50 cc. of chloroform. Shake the combined chloroform extracts with 20 cc. of water and 3 cc. of ammonia solution. Separate, and extract the aqueous liquid with two quantities each of 15 cc. of chloroform. Distil off the chloroform, taking the usual precautions to prevent decrepitation of the strychnine. Dry at 115° C., and wash the residue with three quantities each of 2 cc. of ether; dry and weigh. Wash again with ether, and if the weight is not constant give further washings until no more quinine is removed.

Easton's syrup [3] increases in S.G. on storage on account of the inversion

[1] Harvey and Back, *Analyst*, 1921, **46**, 188. [2] Evers, *Y.B.P.*, 1922, 409.
[3] Evers and Caines, *Y.B.P.*, 1925, 406.

of the cane sugar. It is very readily oxidised by exposure to air, with formation of ferric phosphates.

Syr. Scillæ, B.P.—Syrup of squill contains 175 cc. vinegar of squill in 1000 gm. S.G. about 1·34.

Acetic Acid.—Titrate 20 gm. with $N/2$ sodium hydroxide to thymol blue or phenolphthalein. 1 cc. $N/2$ NaOH ≡ 0·3 gm. acetic acid. Not less than 1 per cent. should be present.

SECTION IX.

TINCTURES.

TINCTURES are liquid preparations made by extracting drugs with alcohol of varying strength. They are much more dilute than liquid extracts. Generally 10 parts of tincture by volume are equivalent to 1 part by weight of the drug, but there are exceptions to this. The tinctures of ferric chloride and of iodine are not strictly tinctures, being alcoholic solutions of the chemicals.

Specific Gravity.—This is determined in the usual way at 15·5° C. by means of a 50 cc. bottle with a capillary stopper, or one having a narrow neck with a graduation at 50 cc.

Total Solid Matter.—5 cc. are accurately pipetted into a flat-bottomed glass or nickel dish and gently evaporated to dryness. The residue is dried in the steam oven to constant weight. Eschbaum [1] proposes the use of a strip of filter paper over which the liquid is distributed. The paper is then rolled up and dried in the oven. Where glycerin is present the total solid matter cannot of course be determined by evaporation at 100° C. An approximate result for comparative purposes may be obtained by heating at 160° C. until the glycerin is removed, but for more accurate analysis some method such as that of Briggs [2] must be adopted.

Alcohol.—The accurate determination of alcohol in all galenicals is a matter of great importance for excise purposes. The results are expressed as percentages of absolute alcohol by volume or as percentages of proof spirit. *Proof spirit* is defined as "*that which at the temperature of* 51° *by Fahrenheit's thermometer weighs exactly twelve-thirteenth parts of an equal measure of distilled water.*" Proof spirit at 60° F. has S.G. 0·91976, and contains 57·1 per cent. of alcohol by volume.

General Method.—50 cc. of the liquid are pipetted accurately into a Thorpe's distillation flask (fig. 19) at the temperature of the room. (In the case of thick liquids, or where special accuracy is required, the special method of measuring given below should be used.) 75 cc. of water are added and the liquid distilled until the distillate nearly reaches the mark of a 100 cc. graduated flask. The distillate, after thorough mixing, is brought to its original temperature, made up to the mark, and the S.G. taken at this temperature in a 50 cc. bottle having a perforated stopper. The S.G. obtained is corrected to 15·5° C. by means of the table on p. 331, and the percentages of alcohol and proof spirit by volume read off from the special tables for this purpose published by H.M. Stationery Office for

[1] *Ber. Deuts. Pharm. Ges.*, 1918, **28**, 417.
[2] *J. Amer. Pharm. Assoc.*, 1915, **4**, 75.

the Commissioners of H.M. Customs and Excise. 25 cc. of the preparation may be used instead of 50 cc. if desired, adding 100 cc. of water instead of 75 cc.

Special Method of Measuring.—Two quantities each of 50 cc. of the liquid are run into a graduated 100 cc. flask, removing the pipette as soon as the

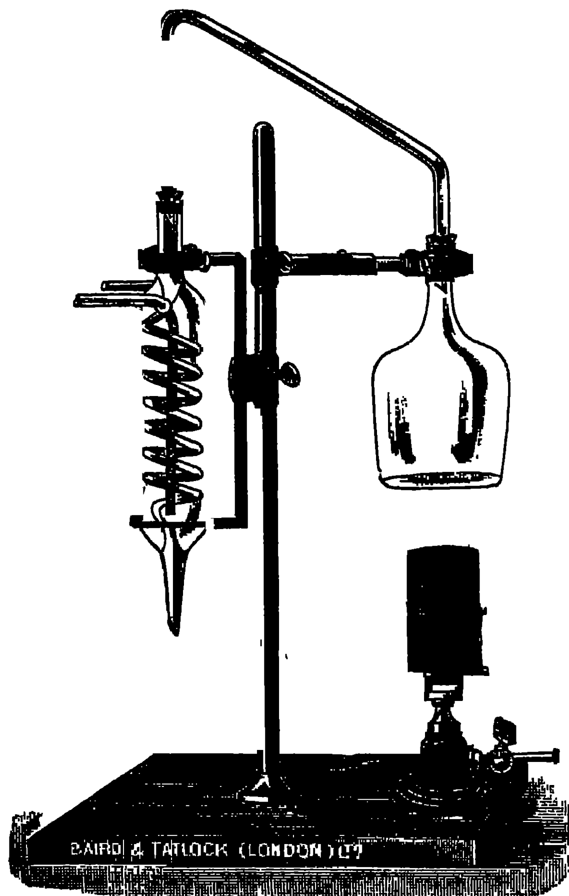


FIG. 19.—Alcohol Distillation Apparatus.

liquid ceases to flow in a stream, and not allowing any single drops to fall in. The liquid is then added drop by drop, counting the drops, until the mark is reached. Then 50 cc. of the liquid are pipetted into the distillation flask in the same way without allowing any single drops to fall in. Half the number of drops required for the 100 cc. are then added, and the method carried on as above.

Certain galenicals require special treatment as follows: When *volatile oils, ether*, or *chloroform* are present, the following method is used. 50 cc. are pipetted into a separator with 50 cc. of brine and 50 cc. of pure petroleum ether. After thorough shaking and separation, the lower layer is drawn off

into the distilling flask, and the petroleum ether layer washed twice with a mixture of 25 cc. of water and 25 cc. of brine, the washings being added to the distilling flask. The distillation is carried out as in the general method.

Preparations which froth may sometimes be prevented from doing so by the addition of a little tannic acid or by the provision of a baffle in the neck of the flask, such as the head of a test-tube brush, to prevent the froth being carried over.

Preparations containing ammonia should be acidified with sulphuric acid before distillation.

Preparations containing volatile acids such as *Tinct. Benzoin, Tinct. Benzoin Co.*, or *Tinct. Ferri Perchlor.*, should be neutralised with sodium hydroxide before distillation after the addition of a little solid phenolphthalein.

When *iodine* is present the liquid should be decolorised with a little powdered sodium thiosulphate before distillation. In the following table are given figures for the most important tinctures. When no limits are given the figures must be taken as approximate. The limits given are the "usual limits," and are not intended to cover abnormal samples.

Tincture.	S.G.	Total Solids. w/v.	Alcohol. v/v.	Remarks.
Tinct. Aconiti, B.P.	0·890–0·900	1·0	67–69	0·04 w/v ether-soluble alkaloids.
„ *Antiperiodica, B.P.C*	0·933–0·939	3·8–5·0	52–57	
„ *Arnicæ Flor., B.P.*	0·952–0·956	2·0–2·6	42–46	
„ *Asafetidæ, B.P.*	0·917–0·921	9·0–13·0	59–64	
„ *Aurant., B.P.*	0·880–0·885	1·9–2·5	74–77	
„ *Belladonnæ, B.P.*	0·895–0·900	1·5–2·0	66–69	0·035 w/v alkaloids.
„ *Benzoin, B.P.C.*	0·857–0·863	6·5–8·5	80–84	
„ *Benzoin Co., B.P.*	0·892–0·900	15·5–19·5	71–75	
„ *Buchu, B.P.*	0·935	4·0	55–58	
„ *Calumbæ, B.P.*	0·916–0·922	0·9–1·1	57–59	
„ *Camph. Co., B.P.*	0·917–0·918	0·25–0·45	57–59	0·5 w/v benzoic acid, 0·05 w/v morphine.
„ *Cannab. Ind., B.P.*	0·841–0·846	3·0–5 0	83–85	
„ *Cantharidini, B.P.*	0·838	0·01	89	1 v/v chloroform, 0·01 w/v cantharidin.
„ *Capsici, B.P.*	0·918–0·920	1·45–1·90	57–59	
„ *Card. Co., B.P.*	0·980–0·990	· 13·5*	37–40	10 v/v glycerin.
„ *Carminativa, B.P.C.*	0·839–0·843	0·4–1·0	85–87	
„ *Cascarillæ, B.P.*	0·903	4	65–68	
„ *Catechu, B.P.*	0·995–1·000	13–15	38–40	
„ *Chiratæ, B.P.*	0·918–0·924	0·95–1·1	56–59	
„ *Chlorof. et Morphin. Co., B.P.*	1·000–1 012	30–33*	53–55	1 w/v morphine hydrochloride, 0·1 w/v hydrocyanic acid.
„ *Cinchonæ, B.P.*	0·915	4–8	65–67	alkaloids 1 w/v.
„ *Cinchonæ Co., B.P.*	0·904–0·910	4–6	65–67	alkaloids 0·5 w/v.
„ *Cinnamomi, B.P.*	0·902–0·909	1·9–3·2	66–68	
„ *Cocci, B.P.*	0·952–0·960	2·0–3·5	42–44	
„ *Colchici, B.P.*	0·895–0·905	1·6–2·1	67–69	
„ *Convallariæ, B.P.C.*	0·920–0·930	1·0	55–58	
„ *Cubebæ, B.P.*	0·840–0·845	2·5	84–87	

* With glycerin.

Tincture.	S.G.	Total Solids. w/v.	Alcohol. v/v.	Remarks.
Tinct. Digitalis, B.P.	0·896–0·905	2·2–2·8	66–69	
" *Ergot. Ammon., B.P.*	0·935–0·950	2·5–5·0	47–51	1 w/v ammonia added.
" *Ferri Perchlor., B.P.*	1·100	..	22·5	5 w/v iron.
" *Gelsemii, B.P.*	0·918–0·924	1·2–1·6	56–59	
" *Gent. Co., B.P.*	0·956–0·966	4·0–5·0	41–44	
" *Guaiaci, B.P.C.*	0·900–0·910	18–20	75–77	
" *Guaiaci Ammon., B.P.*	0·900–0·920	18–20	65–71	2·14 w/v ammonia added.
" *Guaranæ, B.P.C.*	0·935–0·948	5–7	54–57	
" *Hamamelidis, B.P.*	0·948–0·955	1·8–2·5	42–44	
" *Hydrastis, B.P.*	0·920–0·930	2·0–3·0	55–59	
" *Hyoscyami, B.P.*	0·898–0·908	2·0–3·2	65–69	
" *Iodi Fort., B.P.*	0·984–0·987	..	75–78	10 w/v iodine, 6 w/v potassium iodide.
" *Iodi Mitis, B.P.*	0·878–0·879	..	86–88	2·5 w/v iodine, 2·5 w/v potassium iodide.
" *Iodi (Fr. Codex)*	0·900–0·905	..	86–88	2·5 w/v iodine, 6 w/v potassium iodide.
" *Jalapæ, B.P.*	0·910–0·915	..	66–69	1·45–1·55 w/v Jalap resin.
" *Jalapæ Co., B.P.*	0·920–0·930	2·5–3·2	56–58	
" *Kino, B.P.*	0·998–1·005	23–25*	44–46	
" *Krameriæ, B.P.*	0·940–0·950	5·0–7·5	55–59	
" *Lavand. Co., B.P.*	0·834–0·838	0·5–0·8	87–89	
" *Limonis, B.P.*	0·875–0·880	1·3–2·0	75–78	
" *Lobeliæ Ætherea, B.P.*	0·808–0·815	1·8–2·5	55–59	made with *Spt. Ætheris, B.P.*
" *Myrrhæ, B.P.*	0·850–0·856	5–7	83–85	
" *Nucis Vom., B.P.*	0·907–0·910	1·1–1·4	61–64	0·125 w/v strychnine.
" *Opii, B.P.*	0·955–0·965	4·5–6·0	43–45	1·0 w/v morphine.
" *Opii Ammon., B.P.*	0·892–0·896	..	66–69	0·1 w/v morphine, 2 w/v benzoic acid, 2 w/v ammonia added.
" *Persionis, B.P.C.*	0·990–0·996	4·0–6·5	28–31	
" *Podophylli, B.P.*	0·846–0·849	3·5–3·65	86–88	
" *Pruni Virg., B.P.*	0·966–0·976	15	46–50	10 v/v glycerin.
" *Pulsatillæ, B.P.C.*	0·922–0·927	1·7–2·1	56–59	
" *Pyrethri, B.P.*	0·898–0·908	2·1–2·8	66–69	
" *Pyrethri Flor., B.P.C.*	0·940–0·945	5·5–7·0	54–57	
" *Quassiæ, B.P.*	0·945–0·950	0·5–0·7	41–44	
" *Quillaiæ, B.P.*	0·918–0·925	0·9–1·2	56–59	
" *Quininæ, B.P.*	0·885–0·895	3·8–4·4	73–76	2 w/v quinine hydrochloride.
" *Quinin. Ammon., B.P.*	0·926–0·928	..	52–54	2 w/v quinine sulphate, 1 w/v ammonia added.
" *Rhei Co., B.P.*	0·990–0·995	15–16·5*	36–40	10 v/v glycerin.
" *Scillæ, B.P.*	0·955–0 970	9–10	52–56	
" *Senegæ, B.P.*	0·935–0·940	5–7	55–58	
" *Sennæ Co., B.P.*	1·000–1·005	17–20*	36–39	10 v/v glycerin.
" *Serpentariæ, B.P.*	0·920–0·925	2·0–2·5	56–58	
" *Stramonii, B.P.*	0·960–0·970	3·5–5·5	41–44	
" *Strophanthi, B.P.*	0·890–0·897	0·9–1·3	67–69	
" *Tolutana, B.P.*	0·865–0 870	8·0–9·5	81–84	
" *Valerianæ Ammon., B.P.*	0·933–0·944	3–4	50–55	1 w/v ammonia added.
" *Zingiber, B.P.*	0·834–0·837	0·4–0·6	86–89	

* With glycerin.

Tinct. Aconiti, B.P.—*Ether-soluble Alkaloids.*—Evaporate 100 cc. to dryness at a low temperature and continue by the B.P. method for Aconite Root (p. 182). The B.P. requires 0·04±0·002 w/v.

Tinct. Belladonnæ, B.P.—*Alkaloids.*—Evaporate 100 cc. to about 10 cc.; add, if necessary, sufficient alcohol to dissolve any separated matter, and transfer to a separator, rinsing the dish with a little water. Add 10 cc. of water, 20 cc. of chloroform, and 2 cc. of ammonia solution. Shake well, separate, and extract further with two quantities each of 10 cc. of chloroform. Shake the mixed chloroformic solutions with 30 cc. of *N*/3 sulphuric acid. Separate, and shake out with 10 cc. of *N*/3 acid. Mix the acid solutions, add 20 cc. of chloroform and 4 cc. of ammonia. Shake, separate the chloroform, and extract further with two quantities each of 10 cc. of chloroform. Evaporate the chloroform and dry the residue on the water bath for thirty minutes; dissolve it in 10 cc. of *N*/20 sulphuric acid, and titrate back with *N*/20 sodium hydroxide to methyl red. 1 cc. *N*/20 sulphuric acid ≡ 0·01446 gm. alkaloid. B.P. standard, 0·035±0·002 w/v.

Tinct. Benzoin Co., B.P. (Friar's Balsam).—*Total Solid Matter.*—Owing to the presence of volatile aromatic acids or esters the figure for the total solid matter varies according to the time of heating. A more constant value is obtained by adding 1 gm. of ignited light magnesia before drying.

Free and Total Balsamic Acids may be determined by adapting the method given under Balsam of Tolu (p. 187). See Cocking.[1]

Tinct. Camph. Co., B.P. (Paregoric).—Compound tincture of camphor contains 5 v/v of tincture of opium, equivalent to 0·05 w/v of morphine, 0·5 w/v of benzoic acid, 0·3 w/v of camphor, and 0·3 v/v of anise oil.

Benzoic Acid.—Pipette 25 cc. into a beaker, make distinctly alkaline with sodium hydroxide, and evaporate to 10 cc. Shake once with ether and separate the aqueous liquid. Acidify with dilute sulphuric acid, and extract three times with ether. To the mixed ethereal extracts in a separator add 10 cc. of water and 2 drops of methyl red. Add *N*/10 sodium hydroxide until only faintly pink after shaking; then add phenolphthalein, and titrate until pink, shaking after each addition (1 cc. *N*/10 sodium hydroxide ≡ 0·0122 gm. benzoic acid).

Morphine.[2]—Acidify 20 cc. with a few drops of acetic acid, evaporate to dryness, and dissolve the residue in 10 cc. of 60 per cent. alcohol. Evaporate the alcohol, add 10 cc. of water, and a slight excess of lead acetate solution. Make up to 20 cc. and filter off an aliquot portion. Remove the excess of lead acetate with sodium phosphate solution, and to an aliquot portion add potassium hydroxide solution until alkaline, and extract with three portions each of 10 cc. of ether. Wash the mixed ethereal extracts with 1 cc. of potassium hydroxide solution, and add the latter to the alkaline liquid, which is now washed with chloroform, mixed with ammonium chloride solution, and extracted first with a mixture of one volume of alcohol and one volume of chloroform, followed by three or four further extractions with one volume of alcohol and two volumes of chloroform. Evaporate the mixed extracts to dryness, dissolve in 10 drops of *N* sulphuric acid, and make up to 20 cc. Mix 10 cc. with 10 drops of a saturated solution of potassium iodate, allow to stand for five minutes, add 10 drops of strong ammonia solution, and at the end of two minutes compare

[1] Cocking, *Quart. J. Pharm.*, 1928, **1**, 337.
[2] Caines, *Pharm. J.*, 1927, **118**, 751.

the colour with a series of standards prepared from pure morphine. Brindle[1] points out the necessity of neutralising the excess of alkali before the addition of ammonia in the above method.

Tinct. Opii Camphorata, the Paregoric of the U.S.P.; contains 0·4 w/v of opium (=0·04 w/v of morphine), 0·4 w/v of camphor, and 0·4 w/v of benzoic acid.

Tinct. Card. Co., B.P.—Compound Tincture of Cardamoms is coloured with tincture of cochineal. Since the value of this tincture depends as much on its colouring value as on its carminative properties, it is important that the colour should be reasonably uniform. Unfortunately, cochineal varies considerably in colouring power, and slight variations in the *p*H value of the tincture cause differences in the shade of the resulting tincture. A determination of the colour of the tincture in a tintometer is therefore desirable.[2]

Tinct. Cinchonæ, B.P., may be examined for alkaloids in the same way as *Ext. Cinchonæ Liq.* The B.P. method, however, is not very satisfactory, and the U.S.P. method gives better results (see p. 242). B.P. limits, 1±0·05 w/v total alkaloids.

Tinct. Cinchonæ Co., B.P.—*Alkaloids* may be determined as in *Tinct. Cinchonæ*. B.P. limit, 0·5±0·05 w/v total alkaloids.

Tinct. Colchici, B.P., is not standardised, but the U.S.P. tincture, which is of the same strength, is required to contain 0·036 to 0·044 w/v of colchicine. It is assayed by the following process: Evaporate 150 cc. of the tincture to about 15 cc., cool, and dissolve the residue in sufficient distilled water to make 290 cc. Add 10 cc. of solution of lead sub-acetate, and shake frequently during an hour. Filter off 200 cc. (=100 cc. of tincture), and proceed as under the U.S.P. assay of Colchicum Seeds (p. 194).

Tinct. Ergot. Ammon., B.P.—*Colour Test.*—Extract 2 cc. with ether, and carry out the test as described under *Ext. Ergot. Liq.* (p. 242).

Tinct. Ferri Perchlor., B.P. *Iron.*—Dilute 5 cc. with 100 cc. of water and boil. Add excess of ammonia and determine the iron as Fe_2O_3 in the usual manner. $Fe = Fe_2O_3 \times 0{\cdot}6994$.

The U.S.P. gives the following method for *Tinct. Ferri Chloridi*, U.S.P.: Weigh about 5 cc. of the tincture, transfer to a tall beaker, and evaporate to dryness. Add 2 cc. of hydrochloric acid and 5 cc. of hydrogen peroxide solution, and again evaporate to dryness. Dissolve the residue in 3 cc. of hydrochloric acid and transfer to a 250 cc. stoppered flask. Continue as under *Liq. Ferri Perchlor.* (p. 251).

Tinct. Hyoscyami, B.P., is not standardised, but *Tinct. Hyoscyami*, U.S.P., is required to contain 0·0055 to 0·0075 gm. of alkaloids. The tincture is assayed by the same method as given under *Tinct. Belladonnæ*, using 250 cc. of the tincture and evaporating to about 25 cc.

Tinct. Iodi Fort., B.P. *Iodine.*—Dilute 25 cc. to 100 cc. with water, and titrate as for *Tinct. Iodi Mitis*.

Potassium Iodide as under *Tinct. Iodi Mitis*.

Tinct. Iodi Mitis, B.P. *Iodine.*—Titrate 10 cc. with *N*/10 sodium thiosulphate to starch. 1 cc. *N*/10 thiosulphate ≡ 0·012695 gm. iodine.

Potassium Iodide.—Evaporate to dryness, heat at 100° C. until all iodine is removed, and weigh the residue. The addition of alcohol to the

[1] *Pharm. J.*, 1927, 119, 608.
[2] See also Bennett and Middleton, *Y.B.P.*, 1926, 355.

residue assists in the removal of iodine. The potassium iodide in the residue may be determined as under Potassium Iodide (p. 97). Alternatively, the iodine may be removed by diluting 5 cc. with 100 cc. of water and boiling the solution until all the iodine is eliminated.

Tinct. Jalapæ, B.P.—The B.P. requires that when 10 cc. of the tincture, concentrated by evaporation, are mixed with eight times the volume of water, the resin thus separated, washed with water and dried at a gentle heat, shall weigh not less than 0·145 or more than 0·155 gm.

Tinct. Nucis Vom., B.P. *Strychnine.*—Evaporate 50 cc. to a syrupy extract, and carry on as described under *Ext. Nucis Vom. Liq.* (p. 243). B.P. standard, 0·120 to 0·130 w/v strychnine. *Tinct. Nucis Vom.*, U.S.P., contains 0·237 to 0·263 w/v total alkaloids.

Tinct. Opii, B.P. *Morphine.*—The B.P. gives the following method for the determination: Pour 40 cc. into a porcelain dish and evaporate until the volume is reduced to about 10 cc.; mix the residual liquid in a mortar with 1 gm. of freshly slaked lime; dilute the mixture with water to 41 cc.; set aside for half an hour, stirring from time to time. Filter off 25 cc. of the liquid (=25 cc. of tincture) through a plaited 10 cm. filter, add 2·5 cc. of alcohol (90 per cent.) and 15 cc. of ether; shake the mixture; add 1 gm. of ammonium chloride, shake well and frequently during half an hour; set aside for twelve hours for the morphine to separate. Continue the process as described under Opium (p. 207). B.P. standard, 1·0±0·05 w/v.

Tinct. Opii, U.S.P., has the same strength and is assayed as for Opium (U.S.P.), using 80 cc. of the tincture.

Tinct. Opii Ammon., B.P. *Morphine and Benzoic Acid.*—See *Tinct. Camph. Co.*

Tinct. Quininæ, B.P. *Quinine.*—See *Tinct. Quininæ Ammon.* below. Quinine hydrochloride=anhydrous quinine×1·2236.

Tinct. Quininæ Ammon., B.P. *Ammonia.*—Titrate 20 cc. with $N/2$ hydrochloric acid to methyl red. 1 cc. $N/2$ HCl ≡ 0·0085 gm. NH_3. Not less than 0·95 w/v should be present.

Quinine.—Place 50 cc. of water and 20 cc. of chloroform in a separator, and add 10 cc. of the tincture from a pipette, with gentle shaking. Shake, separate the chloroform, and extract with two further quantities each of 10 cc. of chloroform. Distil off the chloroform, dry the residue at 110° C., and weigh as anhydrous quinine. Quinine sulphate (B.P.)=anhydrous quinine×1·36. B.P. strength, 2 w/v of quinine sulphate.

Tinct. Stramonii, B.P., is not standardised, but the U.S.P. tincture is required to contain 0·0225 to 0·0275 w/v of alkaloids, as determined by the same method as is used for *Tinct. Belladonnæ.*

Tinct. Valerian Ammon., B.P. *Ammonia.*—Distil 10 cc. diluted with 75 cc. of water into excess of $N/10$ hydrochloric acid, and titrate back with $N/10$ sodium hydroxide to methyl red. 1 cc. $N/10$ HCl ≡ 0·0017 gm. NH_3.

Tinct. Zingiber, B.P.—The U.S.P. gives the following test for capsicum or other pungent substitute: Evaporate 10 cc. of the tincture to dryness in a small flask. Add 5 cc. of $N/2$ alcoholic potassium hydroxide and boil gently for thirty minutes under a reflux condenser. Evaporate the alcohol on a water bath. Then add 50 cc. of water, shake, filter, and shake out the filtrate with 25 cc. of ether. Evaporate the ether spontaneously by allowing it to drip on to a watch-glass and cautiously apply the tip of the

tongue to the dry residue. The taste should be slightly camphoraceous, but not sharp or bitingly pungent.

"**Concentrated Tinctures.**"—These preparations are sold for diluting with alcohol of appropriate strength in order to produce preparations resembling the official tinctures. They are of varying concentrations, from twice to ten times as strong as the diluted tinctures. When diluted in accordance with the directions they should give products having the appearance and analytical characteristics of the official tinctures. They cannot, however, be regarded as producing true substitutes for the official tinctures.

SECTION X.

MISCELLANEOUS PHARMACEUTICAL PREPARATIONS.

Acetum Scillæ (Vinegar of Squill).—Vinegar of squill is prepared by macerating 1000 gm. of bruised squill with 1000 cc. of B.P. acetic acid, and 3200 cc. of distilled water for seven days. The mixture is then pressed and filtered. S.G. about 1·070. The B.P. requires that 10 cc. shall require for neutralisation to phenolphthalein not less than 21·6 cc. of $N/2$ sodium hydroxide solution. 1 cc. $N/2$ NaOH ≡ 0·03002 gm. $CH_3.COOH$.

Acid Nitro-Hydrochloricum Dilutum, B.P.—Diluted nitro-hydrochloric acid is made by mixing 60 cc. of nitric acid, 80 cc. of hydrochloric acid, and 500 cc. of distilled water, and keeping for fourteen days in a stoppered bottle before use. S.G. 1·07.

Titration.—5 cc. should require 26·6 cc. of $N/2$ sodium hydroxide for neutralisation to methyl red or bromophenol blue.

Acid Sulphuricum Aromaticum, B.P.—Aromatic sulphuric acid contains 7 v/v or 12·88 w/v of sulphuric acid, 25 v/v of tincture of ginger, and 1·5 v/v of spirit of cinnamon in 90 per cent. alcohol. S.G. 0·917 to 0·923.

Titration.—5 cc. require not less than 24·9 cc. of $N/2$ sodium hydroxide for neutralisation to methyl red or bromothymol blue. 1 cc. $N/2$ NaOH ≡ 0·0245 gm. H_2SO_4. Alcohol content, 82 to 84 v/v.

Effervescent Preparations.—The large number of effervescent saline preparations on the market are usually composed of various combinations of citric or tartaric acid and sodium bicarbonate, with or without sugar, or magnesium or sodium sulphates. The analysis of these preparations may be carried out by the ordinary methods for carbon dioxide, sucrose, magnesium, sulphate, and tartaric acid.

Citric acid may be determined either alone or in the presence of tartaric acid by the method of Denigès as modified by Gowing Scopes.[1]

Reagent.—51 gm. of mercuric nitrate and 51 gm. of manganese nitrate are covered with 68 cc. of nitric acid. About 100 cc. of water are added, and when the salts have dissolved, the volume is made up to 250 cc. and the solution filtered.

Method.—A quantity of the substance containing not more than 0·04 gm. nor less than 0·001 gm. of citric acid is exactly neutralised with $N/10$ alkali, using phenolphthalein as indicator. 10 cc. of the reagent are added, and the whole diluted to 200 cc. The mixture is boiled under a reflux condenser for three hours, filtered through a weighed Gooch crucible, and the precipitate well washed with cold water. Usually there is a deposit on the sides of the flask, which may be removed by adding 1 or 2 cc. of

[1] *Analyst*, 1913, **38**, 12.

1 per cent. nitric acid, and rubbing with a rod. The precipitate is washed first by decantation and then in the crucible, and is dried in the water-oven for five hours, when the weight will be found to be nearly constant. Further drying usually only reduces the weight by less than 1 mgm. The precipitate is white, with a slight creamy tinge, if it has been prepared properly. If it is at all yellow, basic salts have formed, and the result will be high. The weight of precipitate × 0·1667 = weight of citric acid. Chloride interferes with this method, and, if present, it should be removed by treatment with silver nitrate.

Oxymel, B.P.—Oxymel contains 100 volumes of acetic acid (B.P.), 100 volumes of distilled water, and 500 volumes of purified honey. S.G. 1·27.

Titration.—25 gm. require not less than 32 cc. of $N/2$ sodium hydroxide to phenolphthalein or thymol blue. 1 cc. $N/2$ NaOH ≡ 0·03 gm. $CH_3.COOH$.

Optical Rotation.—Mix 25 cc. with 1 cc. of lead sub-acetate solution, dilute to 100 cc. and filter through animal charcoal; the optical rotation at 15·5° C. is not more than −3·9° in a 200 mm. tube.

Oxymel Scillæ, B.P. (Oxymel of Squill).—This should be prepared by mixing together 200 cc. of vinegar of squill with 500 cc. of purified honey. The S.G. is about 1·29.

Free Acetic Acid.—Take 25 gm. and titrate with $N/2$ sodium hydroxide to phenolphthalein or thymol blue, adding a little water, if necessary. The B.P. requires 11·9 cc. 1 cc. $N/2$ NaOH ≡ 0·03 gm. $CH_3.COOH$.

Optical Rotation.—See Oxymel above.

Pilula Ferri, B.P.—Iron pill is prepared from exsiccated ferrous sulphate and exsiccated sodium carbonate massed with glucose, tragacanth, and gum acacia. It should contain the equivalent of 22·5 per cent. of ferrous carbonate.

Ferrous Iron as Ferrous Carbonate.—Take 10 pills, break them up, removing the coating, if any; add a little sodium bicarbonate and warm gently with dilute sulphuric acid until all the iron is in solution. Cool, and dilute with dilute sulphuric acid to 201 cc. Filter, and (*a*) to 100 cc. of the filtrate add 3 gm. of potassium iodide and allow to stand in a stoppered bottle at 40° C. for half an hour; cool. (*b*) To another 100 cc. of the original filtrate add $N/10$ potassium permanganate until pink and continue as in (*a*). Titrate the liberated iodine in both the solutions with $N/10$ thiosulphate. 1 cc. $N/10$ thiosulphate ≡ 0·01158 gm. $FeCO_3$. Number of cc. used in (*b*) less number of cc. used in (*a*) = number of cc. due to ferrous carbonate in five pills.[1]

Pilula Hydrargyri, B.P. (Mercury Pill; Blue Pill).—Mercury pill contains 40 gm. of mercury massed with 60 gm. of confection of roses and 20 gm. of powdered liquorice root. The pill mass may be examined microscopically if required.

Mercury.—Heat 0·5 gm. with 10 cc. of sulphuric acid and 3 cc. of nitric acid as in the Kjeldahl process until the solution is colourless, adding a little more nitric acid if the fumes smell of sulphur dioxide. Cool, wash into a porcelain dish, and evaporate on the water bath. Add 15 cc. of water and solution of potassium permanganate until a slight permanent pink remains. Decolorise with a little ferrous sulphate solution, and titrate with $N/10$ thiocyanate using ferric alum as indicator. 1 cc. $N/10$ NH_4CNS ≡ 0·01001 gm. Hg.

[1] See also Liverseege, *C. & D.*, 1927, **106**, 141.

Pulv. Antimonialis (Antimonial Powder).—This powder is required by the B.P. to contain 25 gm. of antimonious oxide to 50 gm. of calcium phosphate.

Antimonious Oxide. Dissolve 0·5 gm. in dilute hydrochloric acid, add 5 gm. of sodium potassium tartrate and a slight excess of sodium bicarbonate. Titrate with $N/10$ iodine to starch. (1 cc. $N/10$ iodine $\equiv$ 0·0072 gm. Sb_2O_3.) The antimony may also be determined by dissolving in $2N$ hydrochloric acid and precipitating with sulphuretted hydrogen. $Sb_2O_3 = Sb_2S_3 \times 0{\cdot}8569$.

The calcium phosphate may be determined in the filtrate by making alkaline with ammonia, and weighing the precipitate.

Pulv. Glycyrrhizæ Co. (Compound Liquorice Powder).—Compound liquorice powder is required by the B.P. to contain senna leaves, 16 gm.; liquorice root, 16 gm.; fennel fruit, 8 gm.; sublimed sulphur, 8 gm., and refined sugar, 52 gm. Moisture should not exceed 6 per cent. The ash in good samples rarely exceeds 4·5 per cent.; about 6 per cent. should be taken as a maximum. Senna, liquorice, and fennel should be looked for microscopically and the absence of adulterations proved. Sulphur may be determined by heating 1 gm. of the powder with 15 to 20 cc. of conc. nitric acid, using a little bromine if necessary. The residue is evaporated after the addition of hydrochloric acid, diluted with water, filtered, and the sulphur determined in the usual way as barium sulphate.[1] It has been suggested, however,[2] that this method gives low results, and that it is sometimes necessary to use potassium chlorate and hydrochloric acid as well as nitric acid during the oxidation process. The presence of exhausted drugs and the approximate amounts of sulphur and sugar may be determined by the method of Liverseege,[3] who extracts the powder first with strongest alcohol (industrial methylated spirits), then with carbon disulphide to obtain the sulphur, and finally with water to obtain the sugar; about 15 per cent. of alcoholic extract should be obtained. The figure for sugar may be a little low owing to slight solubility in the alcohol.

Pulv. Rhei Co., B.P. (Compound Rhubarb Powder).—Compound rhubarb powder is required by the B.P. to contain rhubarb in powder, 22 gm.; light magnesia, 66 gm.; ginger in powder, 12 gm. It is necessary to examine the powder for adulterated or exhausted drugs, for the amount of carbon dioxide, and for correct composition generally.[4]

Moisture.—1 gm. may be dried at 100° C. and the loss in weight noted; this should be not more than 4 per cent. Combined moisture is found by multiplying the carbon dioxide by 0·55.

Ash may be determined on the same amount; the calculated ash, allowing average figures for the ingredients, is 67·5 per cent. The alkalinity of the ash may be determined by titrating with N hydrochloric acid to bromophenol blue (1 cc. N HCl $\equiv$ 0·02016 gm. MgO). The figure so obtained calculated as MgO is usually about 4·5 per cent. less than the ash figure.

Carbon dioxide may be determined by the method of Paul and Cowley as subsequently modified.[6] 0·5 gm. of the powder (or less if much carbonat

[1] Scott, Smith, and Evans, *Analyst*, 1911, 36, 198.
[2] Crosbie and Gibson, *Y.B.P.*, 1915, 127.
[3] *Y.B.P.*, 1906, 269.
[4] Liverseege, Bagnall, and Lerrigo, *Y.B.P.*, 1926, 465.
[5] *Pharm. J.*, 61, 389.
[6] *Y.B.P.*, 1915, 404.

is present) is rubbed down with 3 cc. of water, and washed with two further quantities each of 1 cc. of water into the cup of a nitrometer standing over mercury, and the whole allowed to enter the graduated tube; 5 cc. of concentrated hydrochloric acid are then added, the whole well shaken, and the volume read. This volume is corrected for temperature, pressure, and solubility; the solubility can be found from the following table, which shows that this property depends to a considerable extent on the amount of magnesium chloride present:—

Gm. MgO used.	Cc. of Gas dissolved at 65° C. and 760 mm. by 10 cc. of Acid Solution.
0·00	7·5
0·15	6·3
0·25	6·1
0·35	5·6
0·50	5·1

Working with 0·5 gm. of the powder, the corrected number of cc. of carbon dioxide obtained at 65° C. and 760 mm. multiplied by 0·364 gives the percentage of carbon dioxide in the sample. An amount of powder should be taken such as will give from 2 to 5 cc. of undissolved gas. The amount of carbon dioxide thus found should not exceed 3 per cent. The amount of magnesium carbonate$=CO_2\times 2{\cdot}8$.

Water Extract.—Add 150 cc. of water to 1·5 gm. of the powder, shake continuously for one minute, and pour on to a dry 18½ cm. filter. Return the first few cc. until bright. Evaporate 100 cc. of the filtrate in a flat-bottomed metal dish and weigh after drying in the oven.

Acetic Acid Insoluble Matter.—Add about 120 cc. of approximately $N/2$ acetic acid to 1 gm. of the powder. Shake occasionally during the next day, and filter on the third day, washing with cold water until a colourless filtrate is obtained. Wash the insoluble matter from the filter paper into a tared dish with a jet of hot water, and after evaporation dry in the water-oven for two hours.

Rhubarb and Ginger.—The sum of the water extract and acetic acid insoluble matter multiplied by 1·05 gives the approximate amount of rhubarb and ginger. The organic matter, *i.e.* 100—(ash+total moisture+carbon dioxide) multiplied by 1·19 also gives an approximate figure for rhubarb and ginger. The relative amount of rhubarb and ginger may be approximately gathered from the alcoholic extract of the powder—that for pure ginger being 6 per cent. and for pure rhubarb 33 per cent.[1]

Pulv. Sodæ Tartaratæ Effervescens, B.P. (Seidlitz Powder).—The powder is divided into two packets: No. 1, in blue paper, contains sodium potassium tartrate, 7·5 gm., and sodium bicarbonate, 2·5 gm. No. 2, in white paper, contains 2·5 gm. tartaric acid. The latter may be examined as under Tartaric Acid (see p. 174). The No. 2 powder may be examined as follows:—

[1] *Y.B.P.*, 1915, 403.

Titration.—Weigh out 2 gm., dissolve in water, add 25 cc. of *N*/2 hydrochloric acid, boil off the carbon dioxide, and titrate with *N*/2 NaOH to methyl red. 1 cc. *N*/2 HCl ≡ 0·042 gm. $NaHCO_3$. A second quantity of 2 gm. is ignited as under Potassium Citrate, and titrated. The number of cc. of *N*/2 HCl used in the first titration is subtracted from the number used in the second titration, and the remainder calculated as sodium potassium tartrate. 1 cc. *N*/2 HCl ≡ 0·07055 gm. $NaKC_4H_4O_6, 4H_2O$.

Lead should be tested for in the usual way.

Arsenic should be tested for as under Potassium Carbonate (p. 92).

Spiritus Ætheris, B.P.—Spirit of ether is prepared by mixing ether, 500 cc., with alcohol (90 per cent.), 1000 cc. The B.P. requires a S.G. of 0·802 to 0·806. The actual S.G. of *Spt. Ætheris* prepared with ether of S.G. 0·720 and 90 per cent. alcohol is 0·8023. A difference of 0·001 in the S.G. represents approximately a difference of 1 per cent. of ether.[1]

Spiritus Ætheris Nitrosi (Spirit of Nitrous Ether; Sweet Spirit of Nitre).—This substance is described by the B.P. as an alcoholic solution containing not less than 1·52 or more than 2·66 per cent. by weight of ethyl nitrite, together with aldehyde and other allied substances. It is prepared by distilling alcohol with a mixture of sulphuric and nitric acids over copper turnings into alcohol. S.G. 0·838 to 0·842.

Acidity.—The liquid should effervesce only very slightly on shaking with sodium bicarbonate, showing free acid to be practically absent. 2 cc. diluted to 10 cc. with water should have *p*H value not less than 2·5. The alcohol by the extraction process (p. 266) should be between 82 and 87 per cent.

Aldehyde.—Mix 10 cc. of the solution with 10 cc. of *N*/2 sodium hydroxide in a stoppered cylinder. The liquid should not become brown (only yellow) on standing for twelve hours.

Nitric Oxide.—Shake 2 cc. during five minutes with 2 cc. of a 10 per cent. potassium iodide solution and 2 cc. of dilute sulphuric acid in a nitrometer standing over brine. At N.T.P. not less than 8 or more than 18 cc. of nitric oxide should be produced. Number of cc. of NO × 0·19 = per cent. of ethyl nitrite, w/v. The B.P. requires 1·52 to 2·66 per cent. of ethyl nitrite.

Decomposition.—This preparation is very liable to decompose if kept for a long time or under bad conditions. The greatest care should be taken that old or decomposed samples are not used without previous examination.

Spiritus Ammoniæ Aromaticus (Aromatic Spirit of Ammonia; *Sal Volatile*).—This is an alcoholic solution of ammonia and ammonium carbonate flavoured with oils of lemon and nutmeg. S.G. 0·892 to 0·894. The B.P. limits are low.

Alcohol.—The alcohol may be determined by distillation after making acid with sulphuric acid. 66·5 to 69 v/v should be present.

Total Ammonia.—Run 10 cc. of the spirit into 25 cc. of *N*/2 hydrochloric acid, and continue the titration with the acid to bromophenol blue. 1 cc. *N*/2 HCl ≡ 0·0085 gm. NH_3. The B.P. requires 2·18 w/v of ammonia.

Ammonium Carbonate.—Dilute 20 cc. of the spirit with 25 cc. of water, and add 15 cc. of approximately *N* barium chloride solution. Heat on the water bath for about fifteen minutes, filter, and wash free from alkali.

[1] Milner, *Pharm. J.*, 1927, **118**, 776.

Transfer the precipitate to a beaker, add 50 cc. of *N*/2 hydrochloric acid, boil, cool, and titrate back with *N*/2 sodium hydroxide to methyl red. 1 cc. *N*/2 HCl ≡ 0·0195 gm. B.P. ammonium carbonate, $N_3H_{11}C_2O_5$. The B.P. requires 2·35 to 2·51 per cent. w/v.

Spiritus Ammoniæ Fetidus, B.P. (Fetid Spirit of Ammonia).—This solution is prepared by distilling an alcoholic extract of asafetida and mixing the distillate with ammonia and alcohol. S.G. 0·842 to 0·850. The solution should have a strong odour of asafetida.

Alcohol.—The alcohol may be determined by distillation after making acid with sulphuric acid. Limits, 78 to 81 per cent. by volume.

Ammonia.—Titrate 10 cc. with *N*/2 hydrochloric acid to methyl red. 1 cc. *N*/2 HCl ≡ 0·0085 gm. NH_3. The B.P. requires not less than 2·72 per cent. of ammonia.

Spiritus Camphoræ, B.P.—Spirit of camphor contains 10 w/v of camphor in 90 per cent. alcohol. The B.P. requires a S.G. of 0·845 to 0·850. A solution of 10 w/v camphor in 90 per cent. alcohol has S.G. 0·8471. The difference in S.G. due to a difference of 0·5 per cent. of camphor is 0·00074. Optical rotation at 15·5° C., not less than +4° (B.P.).[1] Refractive index (20° C.), 1·3571. The refractive index is altered by 0·0005 for every 0·5 per cent. of camphor added or subtracted.

Alcohol (after extraction, see p. 266), 80 to 82 v/v.

Spiritus Chloroformi, B.P.—Spirit of chloroform is prepared by dissolving 50 cc. of chloroform in sufficient alcohol to produce 1000 cc. The S.G. of a mixture made in accordance with the B.P. directions, using chloroform of S.G. 1·485, is 0·8650. A difference of 0·5 per cent. of chloroform gives a difference of 0·0033 in the S.G.[2]

Succus Limonis (Lemon Juice).—On account of the fact that it is a natural product, lemon juice is subject to somewhat wide variations in composition. The B.P. requires S.G. 1·030 to 1·040, and between 7 and 9 per cent. w/v of citric acid.

Citric Acid.—Titrate 10 cc. with *N*/2 sodium hydroxide to phenolphthalein. The B.P. requires 20 to 25·7 cc. 1 cc. *N*/2 NaOH ≡ 0·03502 gm. $C_6H_8O_7$. The absence of mineral acids should be ascertained, and also other organic acids which are likely to be cheaper. Commercial samples of lemon juice, although unadulterated, frequently fall below the requirements of the B.P. The total solids are usually somewhat below 10 per cent., and the ash should not be more than 3 per cent. of the solids dried at 110° C. The alkalinity of the ash is equivalent to about 8 cc. of *N*/2 acid per 100 cc. of juice.

Suppositoria Acidi Carbolici, B.P.—Phenol suppositories each contain 0·076 gm. of phenol in a base composed of cacao butter containing a small amount of white beeswax.

Phenol.—Dissolve one suppository in 50 cc. of chloroform and take 10 cc. of the solution. Add about 25 cc. of *N*/10 sodium carbonate, and boil with constant shaking. Cool, add 15 cc. of *N*/10 iodine, shake, and allow to stand five minutes (not more). Add 5 cc. of dilute sulphuric acid, and titrate back with *N*/10 thiosulphate. 1 cc. *N*/10 iodine ≡ 0·001568 gm. phenol. A small allowance must be made for loss in manufacture.

Suppositoria Glycerini, B.P.—Glycerin suppositories contain about 70 per cent. of glycerin and 14 per cent. of gelatine.

[1] Utz, *Pharm. Zentr.*, 1919, **60**, 373. [2] Milner, *Pharm. J.*, 1927, **118**, 776.

Gelatine.—Determine the nitrogen in 1 gm. by the Kjeldahl method. $N \times 7$=gelatine.

Glycerin.—Extract 1 gm. of suppository with alcohol-ether (2 : 1). Evaporate at a low temperature, dry over sulphuric acid, and weigh the glycerin.

Suppositoria Morphinæ, B.P.—Morphine suppositories contain 0·2 gm. of morphine hydrochloride in 12 suppositories, = 0·0126 gm. of anhydrous morphine per suppository.

Morphine.—Dissolve one suppository in 20 cc. of ether in a separating funnel. Wash the ethereal solution with several quantities of *N*/10 sulphuric acid, and make the washings up to 50 cc. Take 10 cc. of this solution, add 10 drops of a saturated solution of potassium iodate, allow to stand five minutes, then add 10 drops of strong ammonia solution, and after two minutes compare the colour with that of a standard prepared in an exactly similar manner and containing 0·0025 gm. of anhydrous morphine. The colours should correspond.

Tablettæ Acidi Acetylsalicylici.—Acetylsalicylic acid tablets, B.P.C., each contain 0·324 gm. (=5 grains) of acetylsalicylic acid. The tablet is usually made by the addition of small quantities of potato starch and sometimes purified talc. The tablets should disintegrate readily in water. Unless the tablets are made with French chalk the ash should be slight.

Free Salicylic Acid.—Dissolve one powdered tablet in 5 cc. of alcohol and dilute to 50 cc. with water. Add 1 cc. of iron alum solution. Not more than a trace of violet colour should appear.

Acetylsalicylic Acid.—Boil three powdered tablets with 50 cc. of *N*/2 NaOH for ten minutes. Cool, and titrate back with *N*/2 HCl to thymol blue or phenolphthalein. Number of cc. *N*/2 NaOH used $\times$0·2317=grains of acetylsalicylic acid per tablet.

Tablettæ Formaldehydi (Formaldehyde Tablets).—The proportion of formaldehyde may be determined by the use of Schiff's reagent.[1] The Schiff's reagent is prepared by grinding 0·2 gm. of powdered fuchsin in a mortar with 10 cc. of water, the solution being poured off and sulphur dioxide gas passed through it to complete saturation. After standing for twenty-four hours the liquid is diluted to 200 cc. with water. For the determination a tablet is weighed, placed in a flask with 200 cc. of water, and boiled under a reflux condenser for thirty minutes, when the liquid and washings from the flask and condenser are made up to 500 cc. and a portion filtered. A standard solution of formaldehyde is prepared by diluting 1 cc. of B.P. solution of formaldehyde to 1000 cc. (1 cc. of diluted solution $\equiv$ 0·00038 gm. formaldehyde). From this solution a series of standards is prepared in ten test-tubes, taking quantities of 0·1 cc. to 1·0 cc. of the standard solution and diluting to 10 cc, with distilled water. 10 cc. of the filtered tablet solution are taken in another test-tube. A second rack, containing an equal number of test-tubes of uniform bore, each containing 2 cc. of the Schiff's reagent, is then prepared. The contents of the tubes in the first rack are poured as rapidly as possible into the tubes holding the Schiff's reagent and immediately mixed thoroughly; after three minutes the colours are sufficiently developed to enable a match to be made. The amount of formaldehyde, in grams, in the tablet is given by the number of cc. of standard solution required, multiplied by 0·019.

[1] Evers and Caines, *Y.B.P.*, 1921.

Trochiscus Acidi Benzoici, B.P. (Benzoic Acid Lozenge).—The content of benzoic acid may be determined by weighing ten lozenges, grinding these up in a mortar, and taking a weight equivalent to about three lozenges. This weight is dissolved in *N*/5 sodium hydroxide solution, filtered, the filtrate transferred to a separator, and washed once or twice with ether, the ethereal washings being discarded. The liquid in the separator is then acidified with sulphuric acid and extracted at least six times with ether, the ethereal washings being bulked and allowed to evaporate spontaneously in a tared dish, the final drying being carried out in the desiccator at the ordinary temperature.[1] The B.P. requires each lozenge to contain 0·03 gm. of benzoic acid.

Trochiscus Acidi Tannici, B.P. (Tannic Acid Lozenge).—The exact determination of the tannic acid content is somewhat difficult, but a very fair result may be obtained by taking advantage of the solubility of tannic acid in alcohol. Five lozenges are ground up in a mortar with about 3 cc. of alcohol (industrial methylated spirit), the grinding is continued with more alcohol, and the paste then transferred to a conical flask, using in all about 50 cc. of alcohol. The flask is covered with a watch-glass and allowed to stand for some hours in a warm place (where the alcohol will be about 10° C. below its boiling-point), with occasional shaking. The alcohol is decanted off through a filter paper, and the solution collected in a porcelain dish. The residue in the flask is treated with a further 50 cc. of alcohol in the same manner, alcoholic solution added to the first, and the flask and filter paper washed once more with alcohol. At least an equal bulk of water is added to the alcoholic extract in the dish, which is then evaporated until all the alcohol has been driven off. The residue is filtered, the filter paper washed with water, and the combined filtrates diluted to about 150 cc. The tannic acid is precipitated by adding 20 cc. of a 5 per cent. solution of copper acetate, the precipitate being washed, ignited, and weighed as copper oxide. Tannic acid$=$CuO$\times$1·305. The B.P. requires each lozenge to contain 0·03 gm. of tannic acid.

Trochiscus Bismuthi Compositus, B.P. (Compound Bismuth Lozenge).—This lozenge is required by the B.P. to contain 0·15 gm. of bismuth oxycarbonate, 0·15 gm. of heavy magnesium carbonate, and 0·30 gm. of precipitated calcium carbonate. Ten lozenges are weighed and ground finely in a mortar, the bismuth being determined by dissolving the ash (which should be obtained with the assistance of a little nitric acid to prevent the volatilisation of metallic bismuth) in hydrochloric acid, adding ammonium chloride, and precipitating as Bi_2O_3 with excess of ammonium hydroxide. The Bi_2O_3 may be filtered off and weighed as such, whilst calcium and magnesium may be determined as usual in the filtrate. $Bi_2O_3 \times 1{\cdot}1111 =$ bismuth oxycarbonate. $CaO \times 1{\cdot}7848 = CaCO_3$; $Mg_2P_2O_7 \times 0{\cdot}6353 =$ heavy magnesium carbonate.

Trochiscus Potassii Chloratis, B.P. (Potassium Chlorate Lozenge).—One lozenge is dissolved in 25 cc. of warm water, about 7 gm. of zinc-copper couple added, and the whole gently heated for an hour, and then boiled for another hour. At the end of this time dilute sulphuric acid is added until the precipitate just dissolves, the liquid is filtered, made alkaline to phenolphthalein with *N*/10 soda, and finally neutralised with very dilute nitric acid until just colourless. The chloride present is then titrated with

[1] *Cf.* benzoic acid, p. 132.

silver nitrate to potassium chromate in the usual way. 1 cc. $N/10$ $AgNO_3 \equiv$ 0·01226 gm. $KClO_3$. The zinc-copper couple may be prepared in the following way: 7 gm. of zinc are washed with $3N$ sodium hydroxide solution and then with dilute sulphuric acid, which is allowed to act for a short time, and finally washed with water. 100 cc. of 3 per cent. copper sulphate solution are added, and the whole heated to 40° to 50° C. for half an hour. The liquid is decanted, and the treatment with copper sulphate repeated. The zinc is very carefully washed with distilled water (care being taken not to remove the deposit of copper), and is then ready for use.

Trochiscus Sulphuris, B.P. (Sulphur Lozenge).—*Determination of Sulphur.*—Two lozenges are ground up to a fine powder and transferred to a fine textured, double thickness, extraction thimble, which has been previously extracted with carbon disulphide. The thimble is then treated with freshly redistilled carbon disulphide in a Soxhlet apparatus for two and a half hours, after which time the flask is removed, the carbon disulphide distilled off, the flask dried for one and a half hours in the water oven, and finally weighed. The increase in weight gives the weight of sulphur in the lozenges taken.

The sulphur may also be determined by gently heating 0·2 gm. of the lozenge in a conical flask with 5 cc. of concentrated nitric acid and 3 cc. of bromine. When the excess of bromine has been removed the whole is diluted with water and precipitated with barium chloride solution as usual. $BaSO_4 \times 0{\cdot}13734$=sulphur.

Potassium Bitartrate.—The residue in the thimble from the above extraction is ignited and the ash so obtained dissolved in water and titrated with $N/10$ hydrochloric acid to bromophenol blue. 1 cc. $N/10$ $HCl \equiv 0{\cdot}0188$ gm. $KHC_4H_4O_6$.

The B.P. lozenge should contain 0·3 gm. of sulphur and 0·06 gm. of acid potassium tartrate.

Vinum Aurantii, B.P. (Orange Wine).—The B.P. describes orange wine as a vinous liquid having a golden sherry colour and a taste and aroma derived from the bitter orange peel. S.G. about 1·040. Total solids, about 15 w/v.; alcohol, 12 to 14 v/v.

Salicylic Acid.—Make 50 cc. slightly alkaline with soda and evaporate to 25 cc. Acidify and extract with ether. Evaporate the ether to dryness, dissolve in water, and test the solution with ferric chloride solution. No violet colour should be obtained.

Sulphites.—Dissolve 1 gm. of sodium bicarbonate in 300 cc. of water in a 500 cc. flask. Add 10 cc. of 20 per cent. phosphoric acid and 25 cc. of orange wine. Distil through a splash-trap into 5 cc. of 10 vol. hydrogen peroxide (free from sulphuric acid). When 150 cc. have collected, acidify with 2 cc. of hydrochloric acid, precipitate the sulphate with barium chloride, and determine as usual. ($SO_2 = BaSO_4 \times 0{\cdot}274$.) It should contain not more than 450 parts per million.

Benzoates.—See Benzoic Acid, p. 132.

Vinum Ferri (Iron Wine).—Iron wine is prepared by macerating iron wire in sherry until the wine contains not less than 0·125 or more than 0·300 per cent. w/v of iron.

Sherry.—The sherry should respond to the tests for purity given on p. 233; salicylic acid need not be tested for.

Iron.—Evaporate 50 cc. to dryness and gently ignite the residue. Heat

the ash with a mixture of equal parts of hydrochloric acid and water, filter and wash. Precipitate the iron in the mixed filtrate and washings with ammonium hydroxide, and weigh as ferric oxide in the usual way. The amount of ferric oxide obtained should be between 0·089 and 0·215 gm. $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

Vinum Ferri Citratis (Wine of Iron Citrate).—This wine is obtained by dissolving 1·8 gm. of iron and ammonium citrate in 100 cc. of orange wine. This corresponds to about 0·6 per cent. of ferric oxide.

Orange Wine.—The wine should respond to the general tests given on p. 281.

Ferric Oxide.—This may be determined by the method given under Vinum Ferri above; about 0·6 per cent. should be present.

Vinum Quininæ (Quinine Wine).—Quinine wine should contain 2 gm. of quinine hydrochloride dissolved in 875 cc. of orange wine.

Orange Wine.—The wine should respond to the general tests given on p. 281.

Quinine.—Take 50 or 100 cc. of the wine, dilute with water and make slightly acid with hydrochloric acid. Extract three times with small quantities of ether; discard the ethereal washings. Make alkaline with ammonia, extract three times with ether, bulk the ethereal extracts, evaporate to dryness in a tared dish, and dry the quinine at 120° C. until constant in weight. Anhydrous quinine × 1·223 = B.P. quinine hydrochloride.

PART VI.

FIXED OILS, FATS AND WAXES.

SECTION I.

INTRODUCTION.

Although it has been thought necessary for the sake of completeness to include in this book an account of the more important fixed oils likely to be met with in pharmacy, it is impossible, in the small amount of space that is available, to present even a short survey of the whole field. The method that has been adopted is to describe briefly the more usual analytical methods and to give under the individual oils, standards, special methods of examination, and tests for likely adulterants. For further information on any of these points the reader is referred to *The Chemical Technology and Analysis of Oils, Fats, and Waxes*, by Lewkowitsch and Warburton, and *Edible Oils and Fats*, by G. D. Elsdon. No attempt has been made to give even a brief account of the constitution of oils or of the theoretical principles underlying the analytical methods.

PHYSICAL METHODS OF EXAMINATION.

The determination of the *refractive index* and *rotatory power* have already been described (pp. 11 and 14).

Determination of Melting-point.—The determination of an exact melting-point for a fat presents considerable difficulty, as the figure obtained depends largely on the conditions of the test, owing to the fact that fats are not definite chemical compounds, but mixtures of glycerides in varying proportions. However, results sufficiently accurate for most purposes are readily obtainable. Fats do not exhibit their normal melting-point for some time after being melted, and therefore, if a sample has been melted, it should be allowed to stand at least twenty-four hours before the melting-point is determined. Two hours in ice may be substituted, except in the case of cocoa butter, which should stand for three days.

The capillary tube method may be used, as described on p. 7, but a simple test, and one which has the additional advantage of possibly being somewhat more accurate, is as follows: An amount of mercury, sufficient to cover the bulb of the thermometer used, is placed in a small basin, which is in turn put into a beaker containing water which can be gradually heated. A small quantity of the fat is placed on the surface

of the mercury. On heating the water in the beaker a point will be reached at which the fat spreads over the surface of the mercury; this is taken as the melting-point. Another method has been suggested by Knapp.[1]

Determination of Specific Gravity.—This may be carried out by any of the methods described on p. 4. The viscosity of the oil sometimes makes the operation rather difficult, and care is needed to exclude air bubbles; persistent air bubbles may often be removed by placing in a vacuum desiccator. For very viscous oils a specific gravity bottle having a fairly wide neck and closed with a watch-glass is sometimes convenient —it is used in a similar manner to the ordinary specific gravity bottle. For liquid oils the temperature 15·5° C. is used, but for oils solid at that temperature, 37·75° C. (100° F.) and 99° or 100° C. are the usual temperatures. For determinations at these higher temperatures the Ostwald pyknometer is the most convenient instrument to use, being immersed in water at the requisite temperature so that only the capillary tubes are uncovered. The temperature of the water, of which the specific gravity is taken as unity, should be distinctly stated—it is usually 15·5° C. The mean correction for temperature has been found by Allen to be 0·00064 for 1° C.[2] The determination of the specific gravity of solid fats and waxes is dealt with on p. 7.

Viscosity.—The viscosity of an oil is of great importance where it is to be used for lubrication, and is often of use in judging its purity. The viscosity of liquid paraffin for internal use is also of great importance. A rough method is to observe the time taken for the oil to run out of a pipette and to compare this with the time taken by an oil of known purity under the same conditions. It is necessary that the temperature should be the same in both cases, as the viscosity depends largely on this. The viscosity of oils for standards and specifications is usually given in terms of the Redwood viscometer. It consists essentially of a vessel, fitted at the bottom with an agate jet of standard dimensions, to contain the oil to be tested, the whole being surrounded by a bath, fitted with a stirrer, which can be heated to any desired temperature. The oil vessel has a stopper consisting of a metal sphere attached to a wire, the sphere resting on a hemispherical cavity in the jet; there is also a small bracket fitted with an upturned point, which serves to indicate the point to which the vessel must be filled with oil. The time (in seconds) which is required for an outflow of 50 cc. is noted (preferably by a stop-watch), the temperature being carefully adjusted. Redwood recommends that the results obtained be compared with those obtained with refined rape oil, by means of the formula—

$$\text{Viscosity} = \frac{n \times 100 \times S}{535 \times 915}$$

where n is the number of seconds recorded and S the specific gravity of the oil.

As a general rule it is more useful to record the actual time of outflow of 50 cc. as determined by experiment at the particular temperature used.

The Valenta Test.—This test depends upon the solubility of oils and fats in acetic acid (S.G. 1·06). 2 cc. each of the oil and the acetic acid are placed

[1] *J. Soc. Chem. Ind.*, 1915, **34**, 1121.
[2] See also Wright, *J. Soc. Chem. Ind.*, 1907, **26**, 513.

together in a test-tube and heated until the mixture becomes clear; the mixture is then allowed to cool, stirring continuously with a thermometer until a point is reached when it again becomes turbid, at which point the temperature is noted. In the case of certain oils the turbidity persists up to the boiling-point of the acid.

The strength of the acetic acid is most easily adjusted by adding water to glacial acid until it gives a temperature of 60° C. with a mixture of several samples of pure butter fat. The test has been critically studied by Fryer and Weston.[1] They observe that moisture and free fatty acids have a large effect on the Valenta figure, so that values must be corrected for these variables. Roughly speaking, 1 per cent. of acidity in the oil, expressed as oleic acid, causes a fall of 2 in the Valenta figure. Fryer and Weston suggest that the acetic acid be standardised so that it gives a figure of 80° C. with neutral almond oil.

CHEMICAL METHODS OF EXAMINATION.

The Determination of Water.—In the case of non-drying and semi-drying oils, 2 gm. of the oil are weighed out into a flat-bottomed metal dish about three inches in diameter, and placed on the boiling water bath for about two hours; the loss in weight is taken as water. In the case of drying oils it is necessary to dry in a wide-mouthed flask closed with a cork carrying two tubes by means of which a current of coal gas or some other inert gas may be passed through. The determination of water in oils by boiling with toluene is the most convenient and accurate method (see p. 179).

The Determination of the Acid Value.—The amount of free fatty acid may be determined by weighing about 10 gm. into a 250 cc. extraction flask, adding about 50 cc. of neutral alcohol (industrial methylated spirit), and warming slightly for a few minutes on the water-oven. A few drops of phenolphthalein or thymol blue solution are then added, and the whole titrated with $N/10$ (or $N/2$) aqueous potassium hydroxide solution—alcoholic potash is unnecessary. The acid value is usually given as *the amount in milligrams of potassium hydroxide which is necessary to neutralise* 1 *gm. of the fat.* 1 cc. $N/10$ KOH $= 0{\cdot}005611$ gm. KOH. The acid value is also expressed as per cent. of oleic acid of which the molecular weight is 282·3. 1 cc. $N/10$ KOH $\equiv 0{\cdot}02823$ gm. oleic acid. Mineral acid may be determined in a similar manner, using water instead of alcohol, and titrating to methyl red.

The Determination of the Saponification Value.

Preparation of Semi-normal Alcoholic Potash.—For general analytical work absolute alcohol need not be used for this purpose, as industrial methylated spirits (non-mineralised methylated spirits) after slight treatment is quite suitable. The action of potash on the untreated spirits is to produce a reddish-brown coloration, but this may be obviated by the following process: Several sticks of potash are added to a Winchester of industrial methylated spirits, and the whole allowed to stand for several days—the longer the better. The spirit is then boiled for several hours under a reflux condenser with the addition of a little potassium permanganate, and finally distilled, the first and last portions being rejected. Alcohol prepared in this way only develops a slight yellow colour on stand-

[1] *Analyst*, 1918, **43**, 3.

ing with potash. An approximately 10N solution of potassium hydroxide can be made by dissolving one pound of the "pure by alcohol" reagent in 700 cc. of water. To prepare $N/2$ alcoholic potash, 50 cc. of this solution are diluted to a litre with the purified methylated spirit, the slight precipitate of potassium carbonate being removed by decantation after standing overnight. The solution will be approximately semi-normal.

The Process.—Approximately 5 gm. of the substance are accurately weighed out into a 250 cc. extraction flask (preferably of resistant glass) and 50 cc. of approximately $N/2$ alcoholic potash added. The same amount of potash solution is run into a second flask containing no oil—this serving as a blank. The flasks are covered with watch-glasses and placed on the boiling water-oven (not in direct contact with the steam) until saponification is complete,[1] this fact being indicated when oil globules are no longer visible. Thymol blue, phenolphthalein, or preferably thymol violet is then added, and the contents of each flask titrated back with $N/2$ HCl. Half these quantities may be used if desired.

The saponification value is the number of milligrams of potassium hydroxide required for the complete saponification of 1 *gm. of the oil.* It is given by the following expression:—

$$\frac{(\text{Cc. for blank} - \text{cc. for oil}) \times 0{\cdot}02805 \times 1000}{\text{Weight of oil used}}.$$

The Determination of the Unsaponifiable Matter.—The term "unsaponifiable matter," used in connection with oils and fats, is usually understood to mean those substances which are insoluble in water and soluble in ether, and which do not combine with alkalis to form soaps. The determination is usually combined with that of the saponification value.

The neutralised soap solution from the determination of the saponification value is made distinctly alkaline, and most of the alcohol is removed on the water bath. The soap is dissolved in about 50 cc. of warm water and the whole transferred to a separator, the final volume being not greater than 100 cc. The solution is cooled, about 50 cc. of ether added, the whole well shaken and allowed to separate. Separation may be hastened by the addition of a little alcohol or potassium hydroxide solution. The extraction is repeated twice more, the ethereal solutions are mixed, washed twice with a small quantity of water, and transferred to a weighed flask. The ether is distilled off, the residue dried at 100° C., and weighed. The addition of a few drops of absolute alcohol to the residue will assist the drying. Bolton[2] suggests drying with sand and extracting with ether in a Soxhlet apparatus.[3]

The Determination of the Iodine Value.—Taking all things into consideration, the best method for the determination of the iodine value of an oil is that due to Wijs. The solution is prepared[4] by dissolving 8 gm. of iodine trichloride and 8·7 gm. of iodine in pure glacial acetic acid on the water bath, and diluting to 1000 cc. with more glacial acetic acid. The oil or fat

[1] In the case of waxes it is necessary to boil under a reflux condenser, using the strongest alcohol, for two hours.

[2] *Oils, Fats and Fatty Foods* (J. & A. Churchill), p. 38.

[3] See also Lester Smith, *Analyst*, 1928, 53, 632.

[4] Iodine chloride, ICl, can be obtained commercially, and the Wijs solution may be made by dissolving 17 gm. of this in 1 litre of glacial acetic acid.

is weighed in a crucible or watch-glass sufficiently small to go into the stoppered flasks or bottles used for the process. The amount of oil taken depends upon its nature—about 0·15 gm. for an oil with an iodine value of 200, and other quantities in proportion. The weight of oil to be used may be calculated from the formula $\frac{42}{\text{highest iodine value expected}}$. The oil is transferred to a well-stoppered flask of about 600 cc. capacity and dissolved in 10 cc. of pure carbon tetrachloride. 25 cc. of the Wijs solution are then added from a delicate pipette—the exact amount need not be known, but the delivery should be made in exactly the same manner each time—the flask is carefully stoppered, and allowed to stand in a dark place for an hour—in the case of drying oils two hours. A blank is put on at the same time using only carbon tetrachloride and Wijs solution. After standing, 10 cc. of a 10 per cent. solution of potassium iodide are added to each flask and about 200 cc. of water. The liberated iodine is then titrated with $N/20$ (or $N/10$) sodium thiosulphate. The percentage of iodine absorbed by the oil, *i.e.* the "iodine value," is given by the following expression:—

$$\frac{(\text{Cc. } N/10 \text{ thiosulphate used for blank—cc. used for oil}) \times 0{\cdot}01269 \times 100}{\text{Weight of oil used}}.$$

The Determination of the Reichert-Meissl Value.—The method about to be described is the modification due to Leffmann and Beam, in which glycerol soda is used for saponification in place of alcoholic soda. It is preferred on account of its rapidity, and also because it is the method used in the Polenske Process, which determination is usually combined with that of the Reichert-Meissl. 5 gm. of the fat are weighed out into a 300 cc. flat-bottomed flask and heated over a naked flame with 15 cc. of glycerol-soda [1] [made by dissolving 1 lb. of caustic soda in a litre of water (approx. $10N$), and mixing 200 cc. of this solution with 700 cc. of glycerol] until saponification is complete, which point is easily seen by the sudden clearing of the solution. The liquid is allowed to cool somewhat, and 135 cc. of hot water are added with continual shaking—this may be run in conveniently from an unstoppered separator marked at 135 cc. 10 cc. of diluted sulphuric acid (100 cc. conc. sulphuric acid in 1000 cc. solution) are then added, together with 0·1 gm. of powdered pumice, which has been passed through a No. 40 sieve. The flask is then attached to the special condenser by means of the Polenske stillhead, and is supported on a piece of asbestos having a hole in the centre, 5 cm. in diameter. The apparatus required can be obtained from any apparatus dealer, and the measurements laid down must be rigidly adhered to in order to obtain correct results. The fatty acids must be entirely melted by a small flame before the distillation is commenced. The distillate is collected in a flask marked at 100 and 110 cc., the flame being so regulated that 110 cc. are collected in twenty minutes (nineteen to twenty-one minutes), and the cooling water supplied at such a rate that the distillate is not above 20° C. The distillate is cooled to 15° C., well mixed by inverting the flask several times, and filtered through a 9 cm. filter. 100 cc. of the filtrate are titrated with $N/10$ sodium hydroxide to phenolphthalein. A blank test should be carried out with the same reagents in exactly the

[1] Leffmann and Beam used 20 cc. of a proportionally weaker soda; the stronger soda only requires about half the time for saponification.

same manner, but using no fat, and the amount so obtained (which should not be more than 0·5 cc.) must be subtracted from each determination. The volume of $N/10$ sodium hydroxide solution, less the figure found in the blank test, is multiplied by 1·1 to give the Reichert-Meissl value.

The Determination of the Polenske Value.—The first part of this process is identical with that given under the Reichert process above. When the flask containing the distillate is removed from under the condenser its place is taken by a 20 or 25 cc. cylinder. When the filtration is completed, 18 cc. of water, measured in the cylinder used, are poured through the condenser into the empty 110 cc. flask placed underneath, which, after allowing time for draining, is then thoroughly shaken and the water poured over the filter paper which has been used to filter the distillate, and, after filtration, rejected. The condenser, cylinder, and 110 cc. flask are then washed out in a similar manner with successive quantities of 20, 15, and 10 cc. of neutral alcohol (industrial methylated spirits), which are finally poured over the filter paper, the mixed alcoholic filtrate being titrated with $N/10$ sodium hydroxide to phenolphthalein. A blank experiment should be carried out in a similar way and the figure subtracted from each determination ; it is not usually more than 0·1.

The Reichert and Polenske values are of use chiefly in the examination of butter, coconut oil, and palm-kernel oil, and the determination of these fats in mixtures. Although ordinary proportion methods are often used in the calculation of the composition of such mixtures, they are very inaccurate owing to the mutual effects of the various fatty acids. For a full account of the methods of calculation and the principles on which they are based the reader is referred to the papers by Cribb and Richards,[1] by Arnaud and Hawley,[2] and later by Elsdon and Smith.[3] A somewhat similar process to that of Polenske has been suggested by Blickfeldt,[4] and is used largely by margarine manufacturers in this country. A modification of these methods is due to Gilmour[5] and to Elsdon,[6] but none of the processes would seem to have any particular advantage over that of Polenske.

The Determination of the Acetyl Value.—*The acetyl value is the number of milligrams of potassium hydroxide which are required to neutralise the acetic acid formed by the saponification of* 1 *gm. of the fat after acetylation.* It is of most value in the examination of castor oil. The following method is due to Benedikt and Lewkowitsch. 10 gm. of the sample are boiled with twice the amount of acetic anhydride for two hours in a round-bottomed flask attached to a reflux condenser by a ground glass joint. The mixture is then transferred to a large beaker containing 500 cc. of water and boiled for half an hour, a slow current of carbon dioxide being passed through to prevent bumping. After standing, the oily layer is separated off and boiled with repeated quantities of water until the last trace of acetic acid (as judged by the acidity of the washings) has been removed. The acetylated product is then dried over anhydrous sodium sulphate and filtered.

5 gm. of the acetylated product are saponified with alcoholic potash,

[1] *Analyst*, 1911, **36**, 327.
[2] *Ibid.*, 1912, **37**, 132.
[3] *Ibid.*, 1925, **50**, 53 ; 1926, **51**, 72 ; 1927, **52**, 63.
[4] *J. Soc. Chem. Ind.*, 1910, **29**, 792 ; 1919, **38**, 1501.
[5] *Analyst*, 1920, **45**, 2.
[6] *Ibid.*, 1927, **52**, 317.

the amount of the latter being measured exactly if the filtration process is used. Next, the alcohol is evaporated off and the soap dissolved in water. From this stage the process may be continued according to (*a*) or (*b*), the latter requiring less time. Both processes give identical results.

(*a*) *Distillation Process*.—The resulting soap is acidified with 10 per cent. sulphuric acid, and the acids distilled in steam until at least 600 cc. are distilled off. The distillate is then titrated with $N/10$ alkali to phenolphthalein or thymol blue.

(*b*) *Filtration Process*.—A quantity of standard sulphuric acid exactly equivalent to the alcoholic potash used is added. The mixture is warmed, whereupon the fatty acids collect on the surface. These are filtered off, washed with water until the washings are no longer acid, and the mixed filtrates titrated with $N/10$ alkali to phenolphthalein. In either process the acetyl value is given by—

$$\text{Acetyl value} = \frac{\text{Cc. of alkali used} \times 5 \cdot 61}{\text{Weight of acetylated oil used}}.$$

The acetyl value of oils which contain volatile or soluble fatty acids will include the alkali required for the neutralisation of these acids. The "true" acetyl value is found by deducting this amount of alkali before the acetyl value is calculated.

The Detection of Cholesterol and Phytosterol.—Cholesterol ($C_{27}H_{46}O$) and phytosterol ($C_{27}H_{46}O$) are alcohols which occur in the unsaponifiable matter of animal and vegetable oils respectively, and form a valuable means of identifying mixtures of these two classes of oils, or of determining to which class a particular oil belongs.

A preliminary microscopic examination is sometimes of value, but decisive results are often only obtained by an application of the *phytosteryl acetate test*.

The unsaponifiable matter from at least 50 gm. of oil is dissolved in ether, the ether allowed to evaporate spontaneously, the residue dried on the water bath, redissolved in the smallest possible amount of absolute alcohol, and allowed to crystallise. The crystals of cholesterol are in thin plates belonging to the rhombic system, whilst phytosterol crystals are of the monoclinic system. When mixtures of the two are present the microscopic characters are of little value.

The phytosteryl acetate test is carried out as follows: The alcoholic solution of the unsaponifiable matter, prepared as in the previous paragraph, is evaporated to dryness on the water bath, and the residue heated with 2 or 3 cc. of acetic anhydride per 100 gm. of the original oil. The excess of acetic anhydride is then evaporated off on the water bath, the residue is heated with the smallest possible quantity of absolute alcohol, and the solution allowed to evaporate spontaneously to crystallisation. The crystals are recrystallised twice and their melting-point taken. Cholesteryl acetate has a melting-point of 114·8° C. (corr.), and phytosteryl acetate a melting-point above 125° C. It is often necessary to crystallise several more times when in the presence of phytosterol the melting-point will rise with subsequent crystallisations. At one time this process was considered to be conclusive, but more recent work, particularly that of Steuart,[1] has shown that whilst vegetable fat in animal fat can be deter-

[1] *Analyst*, 1923, **48**, 155.

mined by this means, the method is useless for determining the presence of animal fat in vegetable fat.

The Titer Test.—This test determines the solidifying point of the mixed fatty acids, and is often of value in the examination of oils. The fatty acids are prepared, and the test is carried out as given below, the method being due to Dalican.

About 50 gm. of the fat are saponified by means of approximately $2N$ alcoholic potash, the alcohol evaporated, and the soap dissolved in water. The solution is then acidified with 10 per cent. sulphuric acid, and the liquid boiled until the fatty acids separate in a clear layer. These are washed free from sulphuric acid with boiling water and filtered through a dry filter paper; if necessary they may be further dried in the desiccator. The acids are melted, and a test-tube $16 \times 3{\cdot}5$ cm. half filled with them. The tube is fastened into the neck of a wide-mouthed bottle, and an accurate thermometer (reading from about $-5°$ to $60°$ C. in fifths of a degree) is placed in the midst of the acids. The mass is well stirred, and readings of the temperature taken every one or two minutes. At first the temperature will fall uniformly, but after a time it will remain stationary, and then rise some tenths of a degree—*the highest temperature reached is the titer of the acids.* A standard method due to Tate was described at the Seventh International Congress of Applied Chemistry.

Colour Tests.—A tremendous amount of work has been published on the identification of oils by the colours produced on the application of certain reagents. A large number of these tests are worse than useless, and may be ignored with advantage, but there are a few that are more reliable, and which, used with care and intelligence, may give valuable assistance; such tests will be described under the oils to which they refer.

It must not be forgotten that many colour reactions depend upon some characteristic impurity in the oil, and that modern conditions of refining tend more and more to eliminate such impurities. Another point of importance is that the manufacturer is often able to treat an oil in such a manner that it will fail to give the characteristic colour reaction for that oil; this applies to Becchi's and Halphen's tests for cotton-seed oil.

The Antimony Trichloride Test for Vitamin A.—This colour test is on rather a different footing from other colour tests in that it is a test for a valuable constituent which occurs in many oils. Though it cannot be said to be definitely proved that the colour is caused by Vitamin A, there is no doubt that the intensity of the colour is proportional to the Vitamin A content, as shown by feeding experiments. The test was originally suggested by Rosenheim and Drummond,[1] who used arsenic trichloride. Carr and Price [2] suggested antimony trichloride, which is more convenient in practice than the arsenic compound.[3]

Antimony Trichloride Solution.—Pure antimony trichloride is washed with a little dry chloroform and dried in a vacuum desiccator. 30 gm. are dissolved in 100 cc. of dry chloroform by gently warming. The solution should be prepared some days before use, and should be kept in a dark amber bottle in the dark. If any thick oil separates, the solution should be decanted from it; otherwise it appears to keep well.

[1] *Biochem. J.*, 1925, **19**, 753. [2] *Ibid.*, 1926, **20**, 497.
[3] See also Wokes and Willimott, *Pharm. J.*, 1927, **118**, 752; *Analyst*, 1927, **52**, 515; Wokes and Barr, *Pharm. J.*, 1927, **118**, 758.

The Test.—A 20 per cent. by volume solution of the oil in dry chloroform is prepared, and 0·2 cc. is run into each of three dry test-tubes. 2 cc. of antimony trichloride solution are added to the first tube, mixed quickly, and poured into the cell [1] of a Lovibond tintometer. The colour is matched as nearly as possible after 30 seconds, and the test is repeated with the second tube and the third, if necessary, so as to obtain a more accurate match. The amount of blue constituent per 1 cm. of thickness is taken as the indication of the intensity of the test.

Other Tests.—Certain tests other than those described above are in more or less general use in the examination of oils and fats, but they lie somewhat outside the scope of this book, and for them the reader is referred to the larger works. Such tests are the *Elaidin test*, the *sulphur chloride test*, the *oxygen absorption test*, the *thermal reactions with bromine and sulphuric acid*, and the *insoluble hexabromide test*. For the latter, however, *cf.* Linseed Oil, p. 204.

[1] The ordinary cells are affected by the reagent. The joints may be protected by paraffin wax. For a special form of colorimeter, see Rosenheim, *Biochem. J.*, 1927, 21, 1329.

SECTION II.

OILS AND FATS.

Almond Oil.—Almond oil has the following analytical characteristics: S.G. 0·915 to 0·920, more usually 0·916 to 0·919; saponification value, 189 to 196; iodine value, 94 to 101; refractive index at 25° C., 1·4685 to 1·4695; acid value, not more than 5·0; M.Pt. of fatty acids, 14° C. This oil is discussed by Lewkowitsch[1] and by Ross and Race.[2] Likely adulterants of almond oil are olive, sesame, cotton-seed, arachis, apricot, and peach-kernel oils.[3] The detection and determination of arachis oil will be dealt with under that heading.

Sesamé and cotton-seed oil would be indicated by a high iodine value and high melting-point of the fatty acids. Almond oil should remain clear on standing for three hours at —10° C.

Apricot and peach-kernel oils are more difficult to detect, as their constants are very similar to those of almond oil, and resource must be had to colour tests. Probably the most characteristic of the several that have been proposed is the one due to Bieber. This test is carried out by shaking five volumes of the oil with one volume of a reagent made by mixing equal weights of concentrated sulphuric acid, fuming nitric acid, and water; pure almond oil is not affected in colour, whilst apricot and peach-kernel oils give a pink coloration of varying intensity; peach-kernel oil gives a much fainter coloration, which is not produced so rapidly as in the case of apricot-kernel oil. A very approximate quantitative result may be obtained by comparing the colour produced by an unknown sample with that obtained with mixtures of known composition, but this is not possible where one does not know which oil is present. Whilst the iodine value of pure almond oil is nearly always less than 100, that of likely adulterants is greater than this. An iodine value greater than 102 almost definitely points to adulteration.[4]

Arachis Oil.—Arachis oil has the following constants: S.G. 0·916 to 0·921; saponification value, 190 to 196; iodine value, 84 to 100; refractive index at 25° C., 1·468 to 1·470; acid value, not more than 5·0; M.Pt. of fatty acids, 28° to 34° C.; titer, 28° to 29·5° C. The distinctive feature of arachis oil is that it contains a fairly constant proportion (about 4·8 per cent.) of arachidic and lignoceric acids, and this fact is taken advantage of to detect and estimate arachis oil in other oils.

The following qualitative test was originally proposed by Bellier, and

[1] *Analyst*, 1904, **29**, 105.
[2] *Ibid.*, 1911, **36**, 263.
[3] The oil known as "peach-kernel oil" is obtained chiefly from apricot kernels.
[4] Cf. *Analyst*, 1928, **53**, 102.

has been modified by various workers. 1 cc. of the oil is saponified with 5 cc. of alcoholic potash (80 gm. of potassium hydroxide dissolved in 80 cc. of water and diluted to 1000 cc. with 90 per cent. alcohol by volume) under a reflux condenser for four minutes. The solution is cooled to 15° C., and 1·5 cc. of acetic acid (1 vol. of glacial acetic acid with 2 vols. of water) are added, and then 50 cc. of 70 per cent. (by volume) alcohol, and the whole shaken with slight warming until the liquid is clear. The liquid is then cooled to 15·5° C. for five minutes, when 5 per cent. of arachis oil in the sample will cause a distinct turbidity. This turbidity is not absolutely characteristic, as certain "residuum olive oils" give a precipitate, so that in all cases where a precipitate is obtained the quantitative test should be applied.

The original quantitative test was devised by Renard,[1] and has been modified by numerous workers, among whom may be mentioned Tortelli, Ruggeri,[2] and Archbutt.[3] A much shorter process was devised by Bellier,[4] but in this sufficient detail was not given in order to obtain accurate results. Bellier's process has been exhaustively tested by Evers,[5] the following process being found to give excellent results. 5 gm. of the sample are saponified for five minutes under a reflux condenser with 25 cc. of alcoholic potash (as used in the qualitative test). 7·5 cc. of acetic acid (1 vol. of glacial and 2 vols. of water) and 100 cc. of a 70 per cent. (by volume) alcohol containing 1 per cent. (by volume) of hydrochloric acid are added to the hot soap solution, and the whole is cooled to 12°–14° C. for one hour. The separated crystals are filtered off and washed with 70 per cent. (by volume) alcohol, containing 1 per cent. of conc. hydrochloric acid (by volume) at 17°–19° C., the cake being broken up with a platinum wire, until the filtrate ceases to give a turbidity with water, the washings being measured. The precipitate is dissolved in 25 cc. to 70 cc., according to its bulk, of 90 per cent. (by volume) alcohol, cooled to a fixed temperature between 15° and 20° C., and allowed to stand at this temperature for about three hours. The crystals are filtered off, washed with a measured volume of 90 per cent. alcohol (about half the volume used for crystallisation), and finally with 50 cc. of 70 per cent. alcohol. They are washed with warm ether into a tared flask, the ether distilled off, and the residue dried at 100° C. and weighed. If the M.Pt. of the residue is lower than 71° C. it is crystallised from 90 per cent. alcohol. Corrections have to be applied for the amount of 90 per cent. and 70 per cent. alcohol used in the process, which corrections may be taken from the tables on p. 294; the second table also contains the factor for the conversion of the amount of arachidic acid found to arachis oil.

Arachis oil is sometimes used for the adulteration of olive oil and almond oil, but is itself liable to adulteration with poppy-seed, cotton-seed, sesamé, and rape oils.

Castor Oil (*Oleum Ricini*, B.P.).—Castor oil is expressed from the seeds of *Ricinus communis*. For pharmaceutical purposes it should be as nearly as possible colourless, and have little objectionable taste. Castor oil has the following characteristics: S.G. 0·958 to 0·970; saponification value, 177 to 187; iodine value, 83 to 90; refractive index, at 25° C.,

[1] *Compt. rend.*, 1871, **73**, 1330.
[2] *J. Soc. Chem. Ind.*, 1898, **17**, 877.
[3] *Ibid.*, 1898, **17**, 1124.
[4] *Ann. Chim. Anal.*, 1899, **4**, 4.
[5] *Analyst*, 1922, **37**, 487.

1·4755 to 1·4785; acid value, not more than 4·0; acetyl value, 147 to 151; M.Pt. of the fatty acids, 13° C.; optical rotation in 200 mm. tube, +7·6° to +9·7°. When cooled for two hours at 0° C. medicinal castor oil should remain clear. The chief characteristics of castor oil are its high and constant acetyl value, its high viscosity, its strong dextro-rotation, and its solubility in alcohol. The acetyl value may be used for an approximate determination of the amount present in mixtures. It should be entirely soluble in all proportions of absolute alcohol, and soluble in 3·5 vols. of 90 per cent. alcohol. The B.P. suggests the following test with petroleum spirit: "10 millilitres shaken with 7 millilitres of petroleum spirit (B.Pt. 50° to 60° C.; S.G. 0·67 to 0·70) in a stoppered glass cylinder form a clear mixture at 15·5° C.; on shaking with a further addition of 3 millilitres of petroleum spirit a turbid mixture is formed which becomes clear when maintained for five minutes at 21° C., but again becomes turbid when the temperature falls below 18° C. (absence of other fixed oils)."

TABLE I.

CORRECTION PER 100 CC. OF 90 PER CENT. ALCOHOL USED FOR CRYSTALLISATION AND WASHING.

Weights of Fatty Acids.	Grams at		
	15° C.	17·5° C.	20° C.
0·1 gm. or less	0·033	0·039	0·046
0·2 " "	0·048	0·056	0·064
0·3 " "	0·055	0·064	0·074
0·4 " "	0·061	0·070	0·080
0·5 " "	0·064	0·075	0·085
0·6 " "	0·067	0·077	0·088
0·7 " "	0·069	0·079	0·090
0·8 " "	0·070	0·080	0·091
0·9 and upwards . . .	0·071	0·081	0·091

TABLE II.

CORRECTION PER 100 CC. OF 70 PER CENT. ALCOHOL USED FOR WASHING.

Weight of Acids Corrected for 90 per cent. Alcohol.	Correction per 100 cc. 70 per cent. Alcohol.		
	M.Pt. 71° C.	M.Pt. 72° C.	M.Pt. 73° C.
	Gm.	Gm.	Gm.
Above 0·10 gm.	0·013	0·008	0·006
0·08 to 0·10 gm.	0·011	0·007	0·006
0·05 to 0·08 "	0·009	0·007	0·005
0·02 to 0·05 "	0·007	0·006	0·005
Less than 0·02 gm. . . .	0·006	0·005	0·004
Factor for conversion of percentage of fatty acids to arachis oil . . .	17	20	22

Chaulmoogra Oil (*Oleum Chaulmoogræ*, B.P.).—Chaulmoogra oil is derived from the seeds of *Taraktogenos Kurzii*. It is sometimes erroneously known as gynocardia oil, but true gynocardia oil is physiologically inactive. The oil of *Hydnocarpus anthelmintica* closely resembles chaulmoogra oil, and has the same action.[1] At ordinary temperatures chaulmoogra oil is a soft, greyish-yellow fat of the consistency of butter and with characteristic odour. Chaulmoogra oil has the following analytical constants: S.G. 25°/15·5° C. about 0·95; saponification value, 198 to 213; iodine value, 96 to 104; refractive index, 25° C.=1·4777 to 1·4785; acid value, 20 to 30; titer test, 39° C.; M.Pt. 22° to 30°; $[\alpha]_D$ (in 10 per cent. chloroform solution) +50° to +52°. The acid value is very variable, and few oils come within the narrow limits given by the B.P. See also Perkins and Cruz.[2]

Cacao Butter.—Oil of theobroma, or cacao butter, is the solid fat expressed from the seeds of *Theobroma Cacao*. It is a pale yellow solid, breaking with a smooth fracture, and having an odour of cocoa. Cacao butter has the following analytical constants: S.G. 15·5° C., 0·990 to 0·998; M.Pt., 28° to 34° C.; saponification value, 190 to 195; iodine value, 33 to 38; refractive index, 40° C., 1·4565 to 1·4580; Reichert-Meissl value, 0·2 to 0·9; titer test, 48° to 49·5° C.; acid value, 1·0 to 2·0. On account of its high price cacao butter may be adulterated with coconut stearin, tallow, and various vegetable oils. The most useful tests are the iodine value, the Reichert value, and the titer test. The acid value should be low.

Solid Paraffin is sometimes used as adulterant; it may be tested for in the same manner as in lard, or the unsaponifiable matter may be determined.

Tallow may be tested for by Bjorklund's method.[3] 3 gm. of the sample are placed in a test-tube, 8·5 cc. of ether (S.G. 0·720) are added, and the tube corked and heated to 18° C.; a clear solution should be obtained. The tube is then immersed in water at 0° C., and the number of minutes noted until the liquid becomes turbid. Bjorklund found that pure cacao butter required 10 to 15 minutes to develop a turbidity, whilst with 5 per cent. of beef tallow a turbidity was produced in eight minutes. Lewkowitsch,[4] however, states that the chief indication to be relied on is the characteristic way in which the crystallisation takes place. In the case of genuine samples, tufts of distinct crystals appear at the bottom and sides of the tube, whilst 5 per cent. of tallow causes the separation of flocks from the cooled solution.[5] The presence of tallow should be corroborated by the *phytosteryl acetate test*.

The presence of so-called "*green butters*" is not so easy to detect; see Halphen,[6] Revis and Bolton,[7] also Tate and Pooley.[8]

Coconut Oil.—Coconut oil up to the present has found little use in pharmacy, but it may be met with as an adulterant of lard or other fats. It has the following analytical constants: S.G. 0·910 to 0·916; saponification value, 245 to 260; iodine value, 8 to 10; refractive index, 40° C., 1·447 to 1·450; Reichert-Meissl value, 6·7 to 7·5; Polenske value, 15 to 20; titer test, 22·5° to 25° C.; M.Pt., 23° to 26° C.; acid value for pharma-

[1] Read, *Pharm. J.*, 1924, **111**, 412.
[2] *Analyst*, 1924, **49**, 236.
[3] *Z. Anal. Chem.*, 3, 233.
[4] *J. Soc. Chem. Ind.*, 1890, **18**, 557.
[5] Cowie and Brandor, *C. & D.*, 1909, **75**, 227.
[6] *Analyst*, 1908, **32**, 468.
[7] *Ibid.*, 1913, **38**, 201.
[8] *Ibid.*, 1921, **46**, 229.

ceutical purposes, not above 6. Coconut oil, along with palm-kernel oil, is distinguished by its high Polenske value and moderately high Reichert-Meissl value, and these two figures are usually used for the determination of coconut oil in mixtures.

The presence of *palm-kernel oil* is a complication, and it is difficult to detect and estimate mixtures of palm-kernel and coconut oils, more especially when other oils are also present. A method has been suggested by Burnett and Revis,[1] based on the temperature at which alcoholic solutions of the barium salts of the insoluble volatile acids become turbid; for details the reader is referred to the original paper.[2]

Where *coconut stearin* is used in admixture with other fats, the Polenske process is seriously interfered with. In such a case the method of Shrewsbury and Knapp may be used with advantage, but the method has been adversely criticised by some. For further particulars the following authors should be consulted—Shrewsbury and Knapp,[3] Ross, Race and Maudsley,[4] Revis and Bolton,[5] and Elsdon.[6]

Cod Liver Oil (*Oleum Morrhuæ*, B.P.).—Cod liver oil is obtained from the liver of the cod, *Gadus morrhua*, by heating with water. The industry is carried on in Norway, Newfoundland, Iceland, and various North Sea ports. Much of the oil on the market is not prepared from pure cod livers, but contains oil from the livers of other species of *Gadus*, such as the haddock or the coalfish. These oils may be detected by an experienced nose, but analytical characteristics are of little value. Norwegian cod liver oil is the best from the point of view of absence of taste and colour. Cod liver oil is a rich source of the vitamins A and D, on which its value chiefly depends. Medicinal oil is refined by cooling and filtering off the stearin which separates.

Medicinal cod liver oil is pale yellow in colour, with a bland, slightly fish-like taste. It has the following analytical constants: S.G. 0·920 to 0·930; saponification value, 179 to 192; iodine value, 155 to 173; refractive index, 25° C., 1·476 to 1·480; acid value, not more than 2·5; Reichert-Meissl value, not more than 0·6; unsaponifiable matter, not more than 1 per cent. in the best oils. When kept at 0° C. for three hours no separation of solid fat occurs. The colour test for Vitamin A (p. 290) should be strongly positive. The most important determinations are the iodine value, the acid value, the Reichert value, and the determination of unsaponifiable matter. A high figure for unsaponifiable matter may indicate, in the absence of mineral oils, the presence of some other liver oils or of shark oil.

Cotton-seed Oil (*Oleum Gossypii Seminis*, U.S.P.).—Cotton-seed oil is a pale yellow, odourless oil, becoming semi-solid at 0° C. It has the following analytical constants: S.G. 0·922 to 0·926; saponification value, 191 to 195; iodine value, 105 to 116; refractive index, 25° C., 1·470 to 1·472; acid value, not more than 2·5; titer test, 33° to 37° C. Cotton-seed oil is not often itself adulterated, but is used for the adulteration of other oils.

Tests.—Many qualitative tests have been proposed for its detection in mixtures, that of Halphen probably being the best. This is carried out as follows: A reagent is made by dissolving 1 gm. of sulphur in 100 cc.

[1] *Analyst*, 1913, **38**, 255.
[2] *Cf.* Elsdon, *Analyst*, 1917, **42**, 298; 1927, **52**, 63.
[3] *Analyst*, 1910, **35**, 385; 1912, **37**, 3.
[4] *Ibid.*, 1911, **36**, 195.
[5] *Ibid.*, 1911, **36**, 334.
[6] *Ibid.*, 1917, **42**, 72, 295, 298.

of carbon disulphide, and adding to this 100 cc. of amyl alcohol; 2 cc. of the oil are mixed with 4 cc. of the reagent, and heated in an oil bath at 110° C. for about fifteen minutes; the production of a red colour indicates the presence of cotton-seed oil. 5 per cent. of cotton-seed oil may be readily detected in this way.

The Halphen test is not given by cotton-seed oil which has been heated to 250° C., so that failure to give the reaction does not necessarily indicate the absence of cotton-seed oil. As a confirmatory test, which is given by heated oils, Lewkowitsch recommends shaking the oil with an equal volume of nitric acid (S.G. 1·375), when a quantity of cotton-seed oil over 10 per cent. will be shown by the production of a coffee-brown coloration. It should not be forgotten that the fat from animals fed on cotton-seed cake will often give the Halphen reaction; such oils, however, do not respond to the phytosteryl acetate test. Kapok oil also gives the Halphen test.

Croton Oil (*Oleum Crotonis*, B.P.).—Croton oil is a brownish-yellow oil expressed from the seeds of *Croton tiglium*. It has a disagreeable odour and acrid taste, and blisters the skin. It is a violent purgative. Croton oil has the following analytical characteristics: S.G. 0·940 to 0·960; saponification value, 210 to 215; iodine value, 102 to 106; refractive index, 25° C., 1·475 to 1·478; Reichert-Meissl value, 12 to 13; optical rotation, +7·9° to +8·2°; acetyl value, 20 to 35; titer test, 19° C.

It is miscible with half its volume of absolute alcohol and is soluble in all proportions in petroleum ether. The B.P. adds: "Thickens slightly, but does not solidify, either completely or partially, when vigorously shaken with half its volume of fuming nitric acid, and the same proportion of water (absence of other non-drying oils)."

Lard (*Adeps Præparatus*, B.P.).—Prepared lard has the following analytical characteristics: S.G. at 15·5° C., 0·934 to 0·938, at 100°/15·5° C., 0·859 to 0·864; saponification value, 192 to 198; iodine value, 52 to 63; refractive index, 40° C., 1·458 to 1·460; Reichert-Meissl value, 0·2 to 0·7; titer test, 42° C.; unsaponifiable matter, not more than 0·5 per cent. Lard contains 0·2 to 0·3 per cent. of unsaponifiable matter, which is chiefly cholesterol. It should melt to a perfectly clear liquid, and should contain no water. The B.P. requires that "water boiled with it does not acquire an alkaline reaction (absence of alkalis), and after filtering and acidifying with nitric acid, does not yield any reaction with solution of silver nitrate (absence of chlorides)." Hard paraffin has been added to lard to give consistency and to mask other additions. As little as 0·5 per cent., or even less, may be detected by Shrewsbury's method. 5 cc. of the lard are saponified with glycerol-soda in the usual way, and then 50 cc. of alcohol (industrial methylated spirit) are added; in the presence of paraffin a turbidity is produced, and on cooling, the paraffin settles out as flakes. In all cases a pure lard should be put on at the same time for comparison. In doubtful cases the determination and examination of the unsaponifiable matter should be carried out.

The usual adulterants of lard are cotton-seed oil and stearin, sesamé, arachis, and coconut oils, tallow and beef stearine; vegetable oils may be indicated by a high iodine value, and may be confirmed by the phytosteryl acetate test. Cotton-seed and sesamé oils may be tested for by their appropriate colour tests, arachis oil by the isolation of arachidic acid, and coconut oil by the Reichert and Polenske values.

The detection of beef stearin and tallow is a more difficult matter, and the detection of 5 or even 10 per cent. requires a large experience of pure lards and careful comparison of the sample with mixtures of known composition. The method usually adopted at present is Stocks' modification of Belfield's method,[1] or some modification thereof. The following is an outline of the process, but for further particulars the original paper should be consulted; see also Lewkowitsch.[2]

The crystals obtained from an ethereal solution are compared with those from two standard sets of mixtures, the first consisting of pure lard, melting at 34° to 35° C., with 5, 10, 15, and 20 per cent. of beef stearin, melting at 56° C.; the second of pure lard, melting-point 39° to 40° C., with 5, 10, 15, and 20 per cent. of beef stearin, melting at 50° C. The process is as follows: The melting-point of the sample is determined by the capillary-tube method. Suppose the melting-point is found to be 34° C.; 3 cc. of the melted fat are run into a graduated cylinder of about 25 cc. capacity; 21 cc. of ether are added, and the fat dissolved at 20° to 25° C. 3 cc. of each of the first set of mixtures are treated in exactly the same way. The five cylinders are cooled down to 13° C. and allowed to remain at that temperature for twenty-four hours. An approximate estimate as to the amount of the adulterant is arrived at by reading off the apparent volume of the deposited crystals. The ether is then poured off as far as possible, and 10 cc. of fresh ether at 13° C. are added in each case. The cylinders are again shaken, cooled as before, and the proportion of crystals read off as before. Finally the contents of the cylinders are emptied into weighed, shallow beakers, the ether drained off carefully, the mass allowed to dry for fifteen minutes at 10° C., and weighed. The weight obtained for the sample under examination is compared with the weight of the crystals obtained from whichever of the standards comes nearest to it. The second set of mixtures is used for samples of higher melting-point. The actual presence of beef fat must be proved by microscopical examination; when the characteristic tufts are seen, beef fat is present. No sample of pure lard melting below 39° C. yielded more than 0·011 gm. of crystals under the above conditions. A sample of melting-point 45·8° C. gave, however, 0·146 gm. of crystals.

Adeps Benzoatus, B.P., is prepared by melting 100 parts of lard with 3 parts of benzoin at 60° C. for an hour, and then straining. Benzoic acid may be determined by the usual methods for foods.

Linseed Oil (*Oleum Lini*, B.P.).—Linseed oil is expressed from the seeds of *Linum usitatissimum*. It is a yellowish-brown oil of characteristic odour. It is the most important member of the drying oil group, and on this property of drying depends its chief value. The number of oils likely to be used in its adulteration depends largely on the relative prices of linseed and other seed oils. Resin oils and fish oils are also likely adulterants, especially in the case of boiled oils. Linseed oil has the following analytical characteristics: S.G. 0·931 to 0·936; saponification value, 191 to 195; iodine value, 175 to 204; refractive index at 25° C., 1·477 to 1·480; Reichert-Meissl value, 0·0. After the iodine value, the most important test is the following.

Determination of Insoluble Hexabromides.—This is carried out by

[1] *Analyst*, 1894, 19, 2.

[2] *Chemical Technology and Analysis of Oils, Fats and Waxes* (Macmillan), 5th Ed., ii. 726–738.

Sutcliffe[1] in the following manner[2]: 1 gm. of the oil is weighed into small flask (100 cc. CO_2 flask), and dissolved in 40 cc. of redistilled eth (S.G. 0·720) and 5 cc. of glacial acetic acid. Bromine is added drop drop, the flask and contents being cooled to about 11° C. in running wat Care must be taken that no excessive rise in temperature takes place whi the bromine is being added. When the addition of bromine causes permanent red colour to be produced, the flask is corked and allowed stand in running water all night. The precipitate is filtered off eitl through two tared superimposed filter papers, or better, through a Goo crucible; it is washed with five successive quantities of cooled ether, a dried along with the flask for three hours in the water-oven. It is th weighed. The percentage of bromides obtained must not be interpret apart from the iodine value. Percentage of bromides=I.V. $\times$0·63 − 78.

If difficulty is found in filtering the bromides, fish oil may be prese and this is practically confirmed if they do not melt without decompositi All other drying oils and semi-drying oils yield a much lower percenta of insoluble bromides, so that if a low percentage is obtained, adulterati with other seed oils should be suspected.

Test for Rosin Oil.—Rosin oil may be tested for by the Liebermar Storch test as follows: About 1 cc. of the oil is gently warmed in a te tube with about the same volume of acetic anhydride with contin shaking. After standing, the acetic anhydride layer is drawn off by mea of a pipette, and tested by adding 1 drop of 65 per cent. sulphuric ac In the presence of rosin oil a transient violet coloration is produced. T amount of rosin oil present may be found by a determination of the u saponifiable matter, which should not be more than 1·0 per cent.; mine oil will also be estimated in this manner.

The oil may also be tested for "break" by heating in a test-tube over 200° C.; only a small amount of coagulation should take place. large break would indicate an immature oil. Another useful test is to sha 10 cc. of the oil with 10 cc. of 50 per cent. by volume sulphuric acid ir 25 cc. stoppered cylinder. The mucilage separates out as a black la between the acid and the oil, and should not occupy more than 0·5 If the acid layer is coloured red or has a greenish fluorescence, blown or f oil must be suspected (Ingle).

If linseed oil is to be used for its drying powers a drying test shou be carried out. This is most easily done by spreading a few drops or glass plate and allowing to stand exposed to the air either at ordina temperatures or in the water-oven, and comparing the films obtained a the time taken for drying with that for a standard oil similarly treat The film should not be brittle, but should be tough and elastic. W experience this is a very useful test. Quantitative results for drying c now easily be obtained; for these the reader is referred to the origi papers, Liverseege and Elsdon,[3] and Elsdon and Hawley.[4] The Reiche Meissl value of raw linseed oil has been found by several observers alwa to be nil.

When considering the genuineness or otherwise of linseed oil, due co sideration should be given to the relationship existing between the vari analytical figures. Thus a linseed oil having a high iodine value (

[1] *Analyst*, 1914, **39**, 28. [2] *Cf.* Ingle, *J. Soc. Chem. Ind.*, 1911, **30**, 344.
[3] *J. Soc. Chem. Ind.*, 1912, **31**, 207. [4] *Analyst*, 1913, **38**, 3.

or over) will have a specific gravity of about 0·934 and a refractive index of 1·480, whilst an oil with an iodine value of 178 will have a specific gravity of 0·930 and refractive index of 1·478; oils with other iodine values will have proportionate figures for specific gravity and refractive index.

Mustard Oil (*Oleum Sinapis Expressum*).—Expressed oil of mustard is obtained from both black and white mustard seed. It has a slight odour of the volatile oil of mustard. It has the following analytical characteristics: S.G. 0·919 to 0·924; refractive index, at 25° C., 1·474 to 1·479; saponification value, 173 to 175; iodine value (black), 105 to 110, (white) 92 to 103. The constants obtained for the oils from black and white seeds are very similar, the chief difference being in the iodine value. The difference is caused by the presence of a smaller amount of solid acids in the oil from the white seed.

Olive Oil (*Oleum Olivæ*, B.P.).—Olive oil is the oil expressed from the ripe fruit of *Olea Europæa*. The oil described in the B.P. is for pharmaceutical purposes and is not an edible oil, which should be of better quality. The best oils are moderately deep in colour and of viscous consistency. Oils pale in colour and of "watery" consistency are usually refined "extracted" oils. Much olive oil nowadays is extracted with solvents. With skill and experience smell and taste are reliable means of distinguishing between expressed and extracted oils, but the following test is stated to indicate the presence of the latter.

Test for Extracted Oil.—A mixture of 2 to 3 cc. of the oil with an equal volume of acetic anhydride is heated in a test-tube and shaken for a short time, cooled, and filtered through a small filter wetted with acetic anhydride. In contact with a few drops of concentrated sulphuric acid in a porcelain dish a little of the filtrate yields a cherry-red coloration if extracted oil is present. If the liquid is then treated with a few cc. of water, a more or less intense green coloration appears and subsequently gradually disappears. Olive oil has the following analytical characteristics: S.G. 0·915 to 0·918; saponification value, 188 to 196; iodine value, 80 to 86; refractive index, 1·466 to 1·468; titer test, 17 to 23° C. The acid value of edible oils should not be more than 4·0, and of pharmaceutical oils not more than 6·0.

The unsaponifiable matter does not usually exceed 1 per cent. Admixture with arachis, sesamé, cotton-seed, and rape oil is the most common form of adulteration. (Adulteration with tea-seed oil is said to take place, but it is difficult to detect this.) The first three may be detected by the usual reactions, whilst rape oil would reduce the saponification value. The iodine value of the "solid" fatty acids is said to give excellent results for the detection of rape oil. Further particulars are given under Rape Oil.

Palm Oil.—Palm oil occurs as a semi-solid, orange or reddish-orange fat with a characteristic odour. It has the following analytical characteristics: S.G. 0·921 to 0·924; saponification value, 198 to 202; iodine value, 52 to 57. The melting-point is very variable and indefinite, ranging from 25° to 50° C. Palm oil often contains large amounts of free acid, the acid value varying from 30 to 160 or more. It should be practically free from water and solid impurity (sand).

Palm-kernel Oil.—Palm-kernel oil has the following analytical character-

istics: saponification value, 243 to 250; iodine value, 13 to 17; refractive index, 1·450 to 1·451; Reichert-Meissl value, 5 to 7; Polenske value, 10 to 12.

Palm-kernel oil is very similar to coconut oil in its constitution, and the problem of detecting mixtures of the two is a very difficult one. For a further discussion of this point the remarks under Coconut Oil should be read. The fact should not be lost sight of that palm-kernel stearin is often used, and that this gives lower Reichert and Polenske figures than the original oil.

Rape Oil.—Rape oil or colza oil has the following analytical characteristics: S.G. 0·913 to 0·916; saponification value, 170 to 177; iodine value, 96 to 104; refractive index, 1·470 to 1·472; titer test, 11·5° to 13·5° C.

The chief characteristics of rape oil are its low specific gravity, its low saponification value, and its high viscosity. The special properties are due mainly to the large proportion of erucic acid which it contains. The unsaponifiable matter should not be much more than 1 per cent. This oil is sometimes mixed with, or replaced by, other oils of the same group, particularly ravison oil (Black Sea or wild rape oil). The iodine value of this is higher than that of rape oil, being about 110 to 120. Lewkowitsch recommends the determination of erucic acid as a means of detecting rape oil in other oils.[1]

Sesamé Oil.—Sesamé oil has the following analytical characteristics: S.G. 0·921 to 0·924; saponification value, 188 to 193; iodine value, 104 to 112; refractive index, 1·471 to 1·473; titer test, 22° to 24° C.

Sesamé oil is somewhat dextro-rotatory, the rotation in a 200 mm. tube being about +1·0°. The most characteristic test is that termed the Baudouin reaction, which is usually applied in the manner suggested by Villavecchia and Fabris as follows: 0·1 gm. of furfural is dissolved in 10 cc. of hydrochloric acid (S.G. 1·19). 20 cc. of the oil are added and the whole thoroughly shaken for one minute and allowed to stand. The aqueous layer is coloured red in the presence of even a small percentage of sesamé oil. This test has been exhaustively examined by various workers, and has been found to be thoroughly reliable.

The oil is sometimes adulterated with poppy-seed oil, cotton-seed oil, arachis oil, and rape oil.

Suet (*Sevum Præparatum*, B.P.).—Suet is sheep tallow; the B.P. describes it as "the purified internal fat of the abdomen of the sheep." Prepared suet has the following analytical characteristics: saponification value, 192° to 195°; iodine value, 33 to 46; refractive index at 60° C., 1·449 to 1·451; titer test, 42° to 48° C.; M.Pt. 45° to 50° C. The acid value should be low—the B.P. states 2·0; it should certainly not be higher than this. Admixture with vegetable oils is readily discovered by colour tests, and the application of the phytosteryl acetate test.

"Hardened" Oils.—Hardened or hydrogenated oils are manufactured by the reduction of oils containing large quantities of unsaturated acids. This is brought about by treating the oils with hydrogen in the presence of a catalyst such as finely divided nickel.

The description of these processes and the properties of the resulting fats lie outside the scope of this section. For further particulars the reader is referred to Knapp[2] and to Lewkowitsch (*Oils and Fats*). An important

[1] *Oils, Fats and Waxes* (Macmillan), ii. 257. [2] *Analyst*, 1913, 38, 102.

application of hydrogenation is in the treatment of cod liver oil to remove the taste. It is doubtful, however, whether the taste can be removed at present without reduction of the vitamin content.

MONOGLYCERIDES.

In recent years, synthetic monoglycerides such as monostearin, monopalmitin, etc., have been prepared commercially, and may be used in ointment bases or toilet preparations. They readily form emulsions with water. They consist of glycerin in which one of the hydroxyl groups is condensed with a fatty acid group. They may be readily distinguished analytically by their high acetyl value, due to the two free glycerin hydroxy groups.

SECTION III.

WAXES.

True waxes differ from oils and fats in that they consist of esters formed by the combination of mono- or dihydric alcohols with certain of the higher fatty acids, and that practically no glycerol is obtained on saponification. Although this is the generally accepted definition of a wax, many popular names in general use do not conform to it, thus sperm oil is a wax, Japan wax is a fat, whilst paraffi
of hydrocarbons. Such n..
characteristics, and were given
stances were known.

Only true waxes will be desc
having been described under Paraffin

Beeswax.—Beeswax has the follow
0·958 to 0·970; saponification value,
refractive index at 80° C., 1·437 to 1·4
to 65° C.

Beeswax consists largely of a mixture of cerotic acid and myricyl palmitate. The ratio of ester to free acid has been found to be very constant and to be about 3·7—this number is widely different from that obtained from any of the likely adulterants, as will be seen from the following table due to Lewkowitsch:—

Substance.	Acid Value.	Ester Value.	Ratio Number.
Carnauba wax . . .	2	78	39
Japan wax	20	207	10·8
Insect wax	3	77·4	29·1
Spermaceti . . .	Traces	130	..
Myrtle wax . . .	3	205	68·3
Tallow	4	191	48
Stearic acid, pure . .	195	0	..
,, ,, commercial .	200	0	..
Resin, Austrian . . .	130 to 146	16 to 21	0·13 to 0·14
,, American . . .	154 to 164	29 to 30	0·18 to 0·19
Galipet	138	36	0·26
Paraffin wax, Ceresin . .	0	0	..

Two grades of beeswax are official in the B.P.—"*Cera alba*" and "*Cera flava*." The white wax is obtained by bleaching the natural yellow wax. The yellow wax is completely soluble in chloroform whilst the white wax usually leaves a slight residue.

Test for Paraffin.—For the detection of paraffin,[1] 1 gm. of the wax is saponified over a flame under a reflux condenser for one hour with 10 cc. of $N/10$ alcoholic potash, and 10 cc. of alcohol (industrial alcohol may be used). The flask is taken off the flame and a thermometer inserted and the liquid stirred continuously until at a certain temperature the solution becomes cloudy. This point is very sharp and constant. In the case of pure waxes the cloudiness is followed by immediate precipitation of large flocks; with adulterated samples the clouding is gradual and flocculation does not occur until a lower temperature is reached. In the case of waxes of the East Indian type, 5 per cent. of paraffin will raise the point from 56° C., the figure for pure waxes, to 61°–62° C., and 10 per cent. raises it to 69°–70° C. With waxes of the European type the temperature of clouding rises from 60° C. for pure waxes to 63°–64° C. for 5 per cent. paraffin, and 74°–75° C. for 10 per cent. paraffin.

A large number of samples of Indian beeswax ("Ghedda" wax) give figures which vary enormously from those of "normal" waxes; the cause of this is not yet definitely known. Such waxes cannot be used in pharmacy.

The more usual adulterants of beeswax are given in the above table. It should yield not more than 1 per cent. of its weight to water, showing the absence of an undue amount of honey.

Sperm Oil.—Sperm oil has the following analytical characteristics: S.G. 0·867 to 0·883; saponification value, 120 to 135; iodine value, 80 to 90; refractive index at 25° C., 1·461 to 1·464. Sperm oil is obtained from the head and blubber of the sperm whale. It may be adulterated with hydrocarbons and oils. The only oil which is difficult to detect is arctic sperm oil. Spermaceti is removed from this oil before it is put on the market. Sperm oil is a pale yellow to light brown oil, sometimes depositing spermaceti at ordinary temperatures. High grades of sperm oil are practically odourless, but others are distinctly fishy.

Spermaceti (*Cetaceum*, B.P.).—Spermaceti is obtained from crude sperm oil by expression. It consists essentially of cetyl palmitate. It occurs in glistening white masses of crystalline structure. The addition of a foreign substance causes it to lose its characteristic appearance, so it is not likely to be adulterated. Spermaceti has the following analytical characteristics: S.G. 0·950 to 0·960; saponification value, 122 to 134; iodine value, 3 to 4·5; refractive index at 80° C., 1·433; M.Pt. 44° to 48° C. The small iodine value usually observed is due to the presence of small quantities of sperm oil. Free acids are practically absent, the acid value being not much more than 0·5.

It is a very brittle wax, and easily reduced to powder, especially with the help of a little alcohol. It is soluble in hot alcohol, but on cooling practically the whole separates out.

Wool Wax (Wool Fat; *Adeps Lanæ*, B.P.; Lanoline).—Wool wax is the purified and dried fat of sheep's wool. It is of importance as an ointment base on account of the fact that it can absorb up to 80 per cent. of its weight of water, and that it is readily absorbed by the skin. Two varieties are

[1] Salamon and Seaber, *J. Soc. Chem. Ind.*, 1915, **34**, 461.

official in the B.P., the anhydrous wax, and a wax containing 30 per cent. of water (*Adeps Lanæ Hydrosus*).

Purified wool wax is a pale yellow, somewhat translucent, tenacious and unctuous mass. It has a slight but characteristic odour when rubbed on the skin. It has the following analytical characteristics: M.Pt. 35° to 40° C.; S.G. 0·940 to 0·950; saponification value, 86 to 103; iodine value, 35 to 49 (Wijs, four hours); acid value, not above 1·4.

It is important that the determination of the saponification value and the iodine value should be carried out under fixed conditions or very variable results will be obtained. The saponification value should be determined with normal alcoholic potash, boiling for two hours, and the iodine value should be determined using 0·2 gm. of wool wax to 20 cc. of Wijs solution, allowing to stand for four hours.

The following determinations should also be made: Moisture, ash, and alkalinity of the ash, if any (indicating the presence of soap).[1]

The B.P. has the following tests among others: Melting-point about 40° C. "A solution of 0·2 gm. in 10 cc. of ether remains colourless on the addition of 2 drops of solution of phenolphthalein (absence of free alkali), but becomes deep red on the addition of one drop of *N* sodium hydroxide (limit of free acid). Heated with a solution of sodium hydroxide, no ammoniacal odour is evolved (absence of organic nitrogenous matter). Ash, not more than 0·3 per cent."

[1] See also Richardson and Bracewell, *J. Soc. Chem. Ind.*, 1916, 35, 160.

PART VII.

ESSENTIAL OILS.

SECTION I.

INTRODUCTION.

THE analysis of essential oils has been dealt with very completely by E. J. Parry[1] and by H. Finnemore,[2] to whose treatises readers are referred for a fuller treatment of the subject. In the present work only a brief description of methods of analysis is given, together with the analytical characteristics of oils which are important for pharmaceutical purposes.

The examination of essential oils to a large extent consists in the determination of physical characteristics, combined with comparatively few chemical methods for the determination of the percentage of constituents in certain oils or for the detection of adulterants. The chief difficulty lies in the interpretation of the results obtained. Essential oils generally show considerable variations in their natural characteristics, which are affected by the source of the plant, or by the season or year in which the collection of the oil-bearing portions is made. For these reasons the characteristics of genuine oils must in many cases vary within wide limits, and considerable adulteration may be possible without arousing suspicion in the mind of the analyst.

Moreover, in no class of materials has the art of scientific adulteration been brought to bear with more skill and assiduity than in that of essential oils. Fortunately the skill of the analyst in discovering adulterations and devising means for their detection has been at least equal to that of those who use their scientific knowledge unscrupulously, but new adulterants are continually being introduced, and the analyst should be prepared to meet with one at any moment.

A most valuable asset to the analyst engaged in the examination of essential oils is a trained nose, which will often detect adulteration where ordinary chemical means fail, or at any rate will give an indication of the adulterant to be sought for. No analysis should be considered complete without the additional evidence afforded by the "nose test." The best method of carrying it out is to place two or three drops of the oil on a piece of folded filter paper, expose to the air for ten minutes or so, and then examine the odour, preferably comparing it with an oil which is known to be genuine.

[1] *The Chemistry of Essential Oils*, 3rd Ed. (Scott, Greenwood & Son, London).
[2] *The Essential Oils* (Benn).

PHYSICAL METHODS OF EXAMINATION.[1]

Oils before testing should be clear at 15·5° C., and, if necessary, should be filtered through dry paper in a covered funnel.

Specific Gravity.—This should be determined accurately by means of the specific gravity bottle (see p. 5) at 15·5° C., and compared with water at 15·5° C. Oils which are solid at this temperature are usually determined at 30° C., being compared with water at 15·5° C.

Refractive Index.—This is determined by means of the refractometer (an instrument reading refractive indices directly is to be preferred), as in the case of fixed oils (see p. 11). The temperature usually employed and that at which most of the published results are given is 20° C. The B.P. limits are given at 20° C. unless otherwise stated. The light used is sodium (D line). The correction to be applied for temperature is fairly constant for most essential oils. Schimmel & Co. use a correction of 0·00035 per 1° C., and this is probably not far wrong. The use of a correction, however, is not to be recommended in cases where exact temperature can be attained.

Optical Rotation.—This is observed by means of the polarimeter (see p. 14) at 20° C. on the undiluted oil in a 100 mm. tube using the sodium D line of the spectrum. The observed angle is the optical rotation of the oil. In cases where the colour of the oil makes it impossible to obtain a reading in a 100 mm. tube, a 50 mm. tube may be used, or the oil may be diluted with alcohol before testing. Turbidity may be removed by filtration with or without the addition of kaolin, or, if due to moisture, by filtration through anhydrous sodium sulphate.

Solubility.—The solubility of an essential oil in alcohol of a given strength is often a useful guide to its purity. The strength of the alcohol used should be carefully adjusted, as slight errors may make a considerable difference to the solubility. The temperature should be as near 15° C. as possible. 1 cc. of the oil is measured into a stoppered, graduated, 10 cc. cylinder, and the alcohol added gradually until on shaking a clear solution results. The solubility is then expressed as 1 vol. of the oil in the number of volumes of the alcohol used.

Occasionally an oil will dissolve to a turbid solution which contains no oil drops, but does not become clear on the further addition of alcohol. In many cases, too, an oil dissolves to a clear solution in a small volume of the alcohol, but is thrown out on the further addition of the solvent, and is again dissolved when still more solvent is added.

Solidifying Point.—This determination is of value in the case of a few oils, and is carried out by slowly cooling about 10 cc. of the oil in a test-tube containing a thermometer and a stirrer, enclosed in a larger tube surrounded by cold water to which ice is gradually added. The oil becomes super-cooled, and solidifies suddenly with a rise of temperature during solidification, and the highest point reached is taken as the solidifying point.

Distillation.—The fractionation of essential oils is an important means of examination. Where the constituents are liable to be affected by high

[1] See Report of Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods appointed by the Society of Public Analysts. *Analyst*, 1927, **42**, 530.

temperatures this should be carried out *in vacuo*. It is important, in order to obtain comparative results, that the conditions of the distillation should be as uniform as possible. Flasks of the same size and the same length of neck or number of fractionation bulbs should be used, and the distillation should be carried on at about the same rate (about 1 drop per second being convenient). Fractions are usually collected over selected ranges of temperature and their volumes measured, but it is sometimes more convenient to collect definite fractions of the amount of oil taken, *e.g.* 10 per cent. irrespective of temperature, and subject these to further examination.

Non-volatile Residue.—About 2 gm. of the oil are heated in a flat-bottomed dish on the water bath until no further loss in weight takes place. An amount of non-volatile residue in excess of the normal would indicate the presence of fixed oils or of non-volatile esters.

CHEMICAL METHODS OF EXAMINATION.

Determination of Esters and Ester Value.—*The ester value is the number of milligrams of potassium hydroxide required to hydrolyse the esters in 1 gm. of the oil.* It is determined in the same way as the saponification value of fixed oils (see p. 285). The acid value of essential oils, except in the cases of lavender and bergamot oils, is usually negligible, so that the saponification value may be taken as the ester value, but in the two cases mentioned the acid value should be determined (see below) and subtracted from the saponification value. In order to determine a suitable weight of the oil to use, divide the highest expected ester value into 350. Weigh this number of grams into a flask, and run in 25 cc. of $N/2$ alcoholic potassium hydroxide. The saponification is usually complete in an hour, but certain esters such as terpinyl acetate, bornyl and menthyl valerianates are very slow in saponifying, and require longer periods. Titrate the excess of alkali with $N/2$ hydrochloric acid to thymol violet, thymol blue, or phenolphthalein. Then:

$$\text{Ester value} = \frac{n \times 0{\cdot}02805 \times 100}{w}.$$

$$\text{The percentage of esters} = \frac{n \times a \times 100}{w}$$

where n=number of cc. $N/2$ KOH used in the saponification, w=weight of oil taken, a=one of the following figures: —

1 cc. $N/2$ KOH ≡ 0·076 gm. methyl salicylate
≡ 0·097 gm. sabinyl acetate
≡ 0·098 gm. linalyl, geranyl, or bornyl acetates
≡ 0·099 gm. menthyl acetate
≡ 0·131 gm. santalyl acetate
≡ 0·110 gm. geranyl tiglate.

If the ester value is known, the percentage of ester$=\frac{M \times A}{560}$, where M=M.W. of ester and A=ester value.

A list of molecular weights of esters is appended.

Ester.	M.W.
Geranyl, linalyl, or bornyl acetates .	196
Menthyl acetate	198
Geranyl tiglate	236
Santalyl acetate	262
Sabinyl acetate	194

Determination of Acid Value.—Dissolve 2 gm. of the oil in 5 cc. of neutral alcohol, and titrate with $N/2$ alcoholic KOH. Then—

$$\text{Acid Value}=\frac{n\times0\cdot02805\times100}{w},$$

where n=number of cc. of $N/2$ KOH used and w=weight of oil taken.

Determination of Alcohols.[1]—These are determined by acetylating the oil with acetic anhydride, thus converting the free alcohols into their acetates. From the ester value of the acetylated oil, or from the difference between this and the ester value of the original oil, the free alcohols can be calculated.

Method.—10 cc. of oil, 20 cc. of acetic anhydride, and 2 gm. of fused sodium acetate are boiled for two hours in a flask, the neck of which is ground on to a reflux condenser. The mixture is cooled, and then heated for about half an hour on a water bath with 50 cc. of water, which is separated. The acetylated oil is thoroughly washed by shaking with (1) 50 cc. of brine; (2) 50 cc. of brine containing 1 gm. of sodium carbonate in solution; (3) 50 cc. of brine; (4) 20 cc. of water. The oil is then dried over anhydrous sodium sulphate, and filtered. The ester value is determined as follows:

Weigh out 2 gm. of the oil, add 5 cc. of 90 per cent. alcohol (rectified), and a few drops of phenolphthalein or thymol blue. Run in $N/10$ alcoholic potash drop by drop till alkaline. Add 40 cc. of $N/2$ alcoholic potash and continue as usual. Where only traces of, or no esters are present in the original oil:

$$\text{Percentage total alcohol}=\frac{xy}{20w-0\cdot42x},$$

where x=number of cc. of $N/2$ KOH used, y= M.W. of alcohol, and w= weight of oil taken.

Where esters are present in the original oil:

$$\text{Percentage free alcohol}=\frac{(b-a)y}{0\cdot42(1335-b)},$$

where a=ester value of original oil, and b=ester value after acetylation.

The total alcohol is calculated by adding this figure to the percentage of alcohol contained in the esters in the original oil.

[1] See Reports of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods of the Society of Public Analysts. *Analyst*, 1928, **53**, 214.

The following are the molecular weights of some alcohols :—

Alcohol.	M.W.	Formula.
Geraniol	154·1	$C_{10}H_{18}O$
Linalol	154·1	$C_{10}H_{18}O$
Borneol	154·1	$C_{10}H_{18}O$
Menthol	156·1	$C_{10}H_{20}O$
Citronellol	156·1	$C_{10}H_{20}O$
Santalol	222·2	$C_{15}H_{26}O$
Sabinol	152·1	$C_{10}H_{16}O$

The Determination of Aldehydes.—*Neutral Sulphite Process.*—5 cc. to 10 cc. of the oil, according to the percentage of aldehydes likely to be present, are pipetted into an absorption flask (about 150 cc. capacity and having a long, thin neck, graduated in tenths of a cc.) containing 70 cc. of a 1 in 5 solution of sodium sulphite, and sufficient phenolphthalein solution to give a well-marked pink colour. The flask is heated on the water bath with very frequent and thorough shaking, adding 33 per cent. acetic acid at intervals until the pink colour is just destroyed. When the colour no longer returns, the heating and shaking are continued for a further fifteen minutes. After cooling, the liquid is made up with a sodium sulphite solution until the oily layer can be measured on the scale. The flask is tapped carefully so as to cause all the drops of oil to rise and coalesce with the bulk of the oil. The volume of oil is then read off and the percentage of aldehydes (by volume) calculated. The percentage by weight may be calculated if the S.G. of the aldehyde absorbed and that of the original oil are known. The temperature at which the volume of the unabsorbed oil is read off should of course be the same as that at which the original oil is pipetted.

Bisulphite Process.—5 to 10 cc. of the oil, as before, are pipetted into an absorption flask (see above) and about 10 cc. of a hot 35 per cent. solution of sodium bisulphite are added. The flask is heated on the water bath with frequent shaking, and more sodium bisulphite added gradually until the flask is nearly full and the solid compound at first formed is redissolved. After cooling, the liquid is made up with sodium bisulphite solution until the volume of the unabsorbed oil can be read off on the scale as in the neutral sulphite process.

The neutral sulphite method is the more satisfactory for the majority of oils, and is less troublesome to carry out than the bisulphite process. There are, however, a few oils for which it does not work well, and the results are nearly always somewhat lower than those given by the bisulphite method. The most suitable method to use will be given under the individual oils.

Hydroxylamine Method.—See Lemon Oil (p. 318).

The Determination of Phenols.[1]—5 or 10 cc. of the oil, according to the percentage of phenols likely to be present, are pipetted into an absorption flask containing about 80 cc. of 5 per cent. potassium hydroxide solution. The flask is frequently shaken during half an hour. The liquid is made up

[1] See Reports of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods of the Society of Public Analysts. *Analyst,* 1928, **53,** 214.

with 5 per cent. potassium hydroxide solution until the oily layer can be read on the scale. Any small drops of oil are caused to rise and coalesce with the bulk of the oil by tapping the flask. The volume of the unabsorbed oil is read off after 24 hours and calculated as percentage (by volume) of the original oil.

The Determination of Artificial Esters.—The number and variety of artificial esters which have been used for the adulteration of essential oils is so large that no one method of detection can be applied, and a number of methods must be used, depending on the nature of the ester employed. These cannot all be detailed here, but a few of the more important ones are given.

Artificial esters may often be detected by careful fractionation of the oil, and an examination of the characteristics of the various fractions as compared with those of a normal oil.

An examination of the soaps formed during saponification is a most valuable means of detection of artificial esters. The esters normally occurring in essential oils are chiefly those of acetic, butyric, valerianic, or tiglic acids. These acids are all volatile with steam, so that if the solution of the soaps is acidified and the acid steam-distilled, any non-volatile acids will remain in the distillation flask. In this way esters of citric, oxalic, succinic, tartaric, or the higher fatty acids may be detected. The method is carried out as follows: After the determination of the ester value in the ordinary way, using $N/2$ sulphuric acid for neutralisation instead of $N/2$ hydrochloric acid, a few drops of $N/2$ alcoholic potash are added and the liquid evaporated on the water bath. To the residue 10 cc. of dilute phosphoric acid solution (3·5 cc. of 88 per cent. acid with 100 cc. of carbon dioxide-free water) are added. The flask is at once connected to a steam generator which has been boiling for about half an hour to remove carbon dioxide, and through a trap to a condenser. The volume of the liquid in the flask is kept at about 10 cc. by heating over a flame. When 250 cc. of distillate have been collected, an excess of $N/10$ sodium hydroxide solution is added, and the excess of alkali titrated with $N/10$ hydrochloric acid solution to phenolphthalein. If the amount of alkali used is appreciably less than that used in the original saponification, the presence of esters of non-volatile acids is to be inferred.

The Detection of Glyceryl Acetate.—10 cc. of the oil are mixed with 10 cc. of petroleum ether and 2·5 cc. of alcohol and shaken in a separator with 20 cc. of water. The glyceryl acetate is soluble in the dilute alcohol. The aqueous layer is filtered and 10 cc. are neutralised to phenolphthalein with $N/2$ alcoholic potash. 5 cc. of $N/2$ alcoholic potash are then added, and the liquid boiled for an hour under a reflux condenser. If more than 0·2 cc. of the potash is absorbed, the presence of glyceryl acetate is indicated.

The Detection of Terpinyl Acetate.—Terpinyl acetate is saponified more slowly than the esters normally occurring in essential oils, and this difference is employed for its detection as follows: 2 cc. of the oil are weighed into each of two saponification flasks. To (i) is added 20 cc. of $N/2$ alcoholic potash, and the mixture boiled for exactly two hours and then titrated. To (ii) is added 25 cc. of rectified alcohol and 10 cc. of $N/2$ alcoholic potash, and the mixture boiled for exactly one hour and titrated immediately. The difference in the saponification values found should not be more than 5. Large differences indicate the presence of terpinyl acetate. Other methods of analysis will be found described under the individual oils.

SECTION II.

INDIVIDUAL ESSENTIAL OILS.

Almond Oil, Essential (Oil of Bitter Almonds, *Ol. Amygdalæ Essent.*).—Almond oil consists almost entirely of benzaldehyde, with a small percentage of hydrocyanic acid in combination as the cyanhydrin. This hydrocyanic acid may be removed, when the oil is known as *Ol. Amygdalæ sine Acid. Prussic.*, or S.A.P.

Ol. Amygdalæ Essent. Ang. is distilled from almonds, while *Ol. Amygdalæ Essent. Persic.* is obtained from peach or other kernels, but the oils are indistinguishable chemically.

Characteristics.—S.G. 1·045 to 1·070 ; refractive index, 1·5320 to 1·5450 ; optical rotation, 0° to +0·16°.

Hydrocyanic Acid Determination.—Weigh out 1 gm. of oil into a small flask. Mix 10 cc. of magnesium hydroxide mixture [1] and 40 cc. of water, and titrate with $N/10$ silver nitrate to potassium chromate until reddish. Add this mixture to the oil, and continue the titration with vigorous shaking until a permanent reddish tint is produced. 1 cc. $N/10$ $AgNO_3 \equiv 0{\cdot}0027$ gm. HCN. The U.S.P. requires from 2 to 4 per cent.

Test for Nitrobenzene.—Add 10 drops of oil to a little alcohol, add 2 cc. of acetic acid and a little zinc dust, boil, make alkaline with sodium hydroxide, and add a few drops of chloroform. No odour of phenyl*iso*cyanide should be observed.

Benzaldehyde (U.S.P. method).—Dissolve about 3 cc. of freshly redistilled phenylhydrazine in about 60 cc. of alcohol, and titrate 25 cc. of this solution, which must be freshly prepared, with $N/2$ hydrochloric acid, using 1 drop of methyl orange T.S. as indicator. To about 1 gm. of oil of bitter almonds, accurately weighed, add another 25 cc. portion of the phenylhydrazine solution, and allow the mixture to stand thirty minutes. Add 1 drop of methyl orange T.S., and acidify the mixture by adding a measured excess of $N/2$ hydrochloric acid. Filter the mixture, and wash the precipitate with small portions of distilled water until the washings cease to redden moistened blue litmus paper. Then titrate the excess of hydrochloric acid in the combined filtrates with $N/2$ sodium hydroxide and subtract the number of cc. of $N/2$ hydrochloric acid consumed from the number of cc. of $N/2$ hydrochloric acid used in titrating 25 cc. of the phenylhydrazine solution. The difference, multiplied by 0·05304, gives the weight of benzaldehyde.

Ajowan Oil (Ptychotis Oil).—The oil distilled from the fruit of *Carum copticum.* It is used as a source of thymol.

[1] A suspension of about 5 gm. of freshly precipitated magnesium hydroxide in 100 cc. of water.

Chief Constituent.—Thymol.

B.P. Characteristics.—S.G. 0·910 to 0·930; optical rotation, +1° to +2°; phenols, not less than 40 per cent.

Anise Oil.—This oil may be either distilled from anise fruit (*Pimpinella anisum*), or from the fruit of the star anise (*Illicium verum*). The two oils are practically indistinguishable. The oil congeals at about 15·5° C.

Chief Constituent.—Anethol.

B.P. Characteristics.—S.G. 20°/15·5° C., 0·975 to 0·990; refractive index, 1·554 to 1·560; optical rotation, −2° to +1°.

Solidifying Point.—This is about 15·5° C. (not below 15° C.). For its determination the well-known Beckmann's freezing-point apparatus may be used. This consists essentially of a wide boiling-tube enclosed in a tube of larger diameter, both being in a vessel filled with cold water. The inner tube is provided with a cork carrying an accurate thermometer. The oil is introduced into the inner tube to a depth of about 5 cm. The water in the outer vessel is cooled until the thermometer falls to about 6° to 8° C., when a crystal of anethol is dropped into the oil. Crystallisation occurs and the temperature rises, the highest point being taken as the solidifying point.

Distillation—not less than 80 per cent. distils between 225° and 235° C. *Solubility* in 90 per cent. alcohol, 1 in 3; the S.G. rarely falls below 0·980.

Bay Oil (*Ol. Myrciæ Acris*).—Bay oil is distilled from the leaves of *Pimenta acris*. It is chiefly used for the preparation of bay rhum. The characteristics of a normal distillate are as follows: S.G. 0·965 to 0·985; refractive index, 1·510 to 1·520; optical rotation, —0·5° to —3·0°; phenols, 55 to 68 per cent. Many commercial samples are merely fractions of bay oil, and have a lower S.G. and lower phenol content.

Cade Oil (Juniper Tar Oil, *Ol. Cadinum*).—Oil of cade is an empyreumatic oily liquid obtained by the destructive distillation of the woody portions of *Juniperus oxycedrus*. The chief constituent is cadinene. It should be completely soluble in ether or chloroform, and almost entirely soluble in hot alcohol. On shaking with water the aqueous layer is acid to litmus.

B.P. Test for Pine Tar.—Shake 1 cc. of the oil with 15 cc. of petroleum ether and filter. To the filtrate add an equal volume of copper acetate solution and shake. When the two layers have completely separated, 5 cc. of the upper layer are removed and mixed with 10 cc. of ether. The colour of the solution should be pale brownish-yellow and not green. The S.G. is about 0·990, varying from 0·980 to about 1·0. A considerable fraction should distil from 260° to 280° C.

Cajuput Oil.—Cajuput oil is distilled from the leaves of *Melaleuca minor* and other species of *Melaleuca*. It usually has a green colour due to contamination with copper. Chief constituent, cineol.

Characteristics.—S.G. 0·917 to 0·930; refractive index, 1·465 to 1·471; optical rotation, —1° to —4°; cineol content, 45 to 65 per cent. For the method of determining cineol, see Eucalyptus Oil (p. 316).

Camphor Oil.—Camphor oil is the oil obtained together with camphor by distillation from *Cinnamomum camphora*. Two oils are met with in commerce, the "light," or "white" oil, which consists chiefly of terpenes, and the "heavy," or dark brown oil, which contains safrol. The characteristics of these oils vary according to their origin, and no definite

standards can be laid down. Very little camphor remains in the oils now obtainable.

Characteristics.—Light oils: S.G. 0·870 to 0·900; refractive index, 1·465 to 1·480; optical rotation, +14° to +32°. Heavy oils: S.G. 0·990 to 1·04; refractive index, 1·503 to 1·510; optical rotation, 0° to +12°.

Determination of Camphor.—Fractionate 300 gm., collecting the fractions below 195° C., and that from 195° to 220° C. Place the second fraction in a freezing mixture for one hour, filter off the camphor, and press in a filter cloth for half an hour. Press again for fifteen minutes in filter paper and weigh. Redistil the mother liquor, collect the fraction 205° to 220° C., and freeze as before. Repeat this once more.

Caraway Oil.—The oil distilled from the fruit of *Carum carvi.* Chief constituent, carvone.

Characteristics.—S.G. 0·909 to 0·920; refractive index, 1·484 to 1·490; optical rotation, +75° to +82°; carvone, 50 to 60 per cent.; solubility in 90 per cent. alcohol, 1 in 1; solubility in 80 per cent. alcohol, 1 in 10. The carvone is determined by the sodium sulphite process (see p. 310). On distillation at least 50 per cent. should distil above 200° C.

Cardamom Oil.—The oil distilled from the official cardamom seeds from *Elettaria cardamomum* has the following characteristics: S.G. 0·923 to 0·948; refractive index, 1·462 to 1·469; optical rotation, +24° to +48°; solubility in 70 per cent. alcohol, 1 in 2 to 5; ester value, 90 to 150. Two hours should be allowed for saponification, as terpinyl acetate is present.

Cassia Oil.—The oil is distilled from *Cinnamomum cassia.* Chief constituent, cinnamic aldehyde.

Characteristics.—S.G. 1·055 to 1·070; refractive index, 1·600 to 1·606; optical rotation, −1° to +6°; acid value, 6 to 16. A high acid value indicates the presence of colophony, which was formerly a frequent adulterant. Solubility in 80 per cent. alcohol, 1 in 2; cinnamic aldehyde content, 80 to 95 per cent. The cinnamic aldehyde is determined by the bisulphite process (see p. 310). The neutral sulphite method gives results about 2 per cent. lower.

Cedarwood Oil (*Ol. Cedri Ligni*).—This oil is obtained from the wood of *Juniperus virginiana.*

Characteristics.—S.G. 0·940 to 0·960; refractive index, 1·500 to 1·510; optical rotation, −25° to −44°. The cedarwood oil which is used in microscopy is not the natural oil, but is prepared by distilling off the lighter portion *in vacuo* until the residue has the required refractive index, viz. 1·515.

Chamomile Oil.—The official oil is known as *Roman Chamomile Oil,* and is distilled from the flowers of *Anthemis nobilis.* When freshly distilled it has a blue colour, which changes to green or greenish-brown on keeping. Chief constituents, a number of esters of tiglic and angelic acids.

Characteristics.—S.G. 0·905 to 0·920; refractive index, 1·442 to 1·458; optical rotation, −3° to +3°; acid value, 1·5 to 15; ester value, 220 to 320. Soluble in less than 1 volume of 90 per cent. alcohol, and in 6 volumes of 70 per cent. alcohol.

German Chamomile Oil, distilled from the flowers of *Matricaria chamomilla,* is an oil of quite different character, its ester value being 5 to 30.

Cinnamon Oil.—Cinnamon bark oil is distilled from the bark of *Cinnamomum zeylanicum.* Chief constituent, cinnamic aldehyde.

Characteristics.—The oils which satisfy the requirements of the B.P. are

comparatively few, and therefore wider limits are given here. Owing to different methods of distillation the characteristics of the oils distilled in England are different from those distilled on the Continent, which are heavier and have a higher cinnamic aldehyde content. Some Continental oils are adulterated with cinnamic aldehyde obtained from cassia oil, which can only be detected by its harsher odour. English oil: S.G. 1·00 to 1·04; refractive index, 1·570 to 1·585; optical rotation, 0° to —1°; aldehydes, 58 to 70 per cent.; solubility in 70 per cent. alcohol, 1 in 5. Continental oil: S.G. 1·020 to 1·040; refractive index, 1·585 to 1·591; optical rotation, 0° to —1°; aldehydes, 63 to 76 per cent.; solubility in 70 per cent. alcohol, 1 in 5.

Cinnamon bark oil is sometimes adulterated by the addition of the leaf oil, which may be detected by its influence on the physical characteristics, by its odour, by the blue colour given with ferric chloride, and by the increase in the percentage of phenols, of which not more than 10 per cent. are present in the bark oil.

Cinnamon Leaf Oil has characteristics quite different from the bark oil. The most important constituent is eugenol, cinnamic aldehyde only being present in small amount.

Characteristics.—S.G. 1·043 to 1·066; refractive index, 1·53 to 1·54; optical rotation, —0·2° to +2·5°; eugenol, 70 to 95 per cent.; solubility in 70 per cent. alcohol, 1 in 2 to 3. Cinnamon leaf oil gives a blue colour on the addition of one drop of ferric chloride solution; this test may be used for its detection in cinnamon bark oil.

Clove Oil.—The oil distilled from the dried flower-buds of *Eugenia caryophyllata*. Chief constituent, eugenol.

Characteristics.—S.G. 1·047 to 1·065; refractive index, 1·530 to 1·536; optical rotation, —0·3° to —2·5°; eugenol, 82 to 92 per cent. The B.P. requires not less than 85 per cent. Solubility in 70 per cent. alcohol, 1 in 1 to 3. The eugenol is determined by the method for phenols (p. 310). Clove oil gives a blue colour on the addition of a drop of ferric chloride solution.

Copaiba Oil.—Copaiba oil is the volatile oil distilled from the oleo-resin copaiba (*q.v.* p. 196). The oil differs widely in characteristics according to the variety of copaiba from which it is derived. *B.P. Characteristics:* S.G. 0·896 to 0·910; refractive index, 1·496 to 1·502; optical rotation, —7° to —35°. The chief adulterants of copaiba oil are gurjun balsam oil and African copaiba oil. Gurjun oil has a high lævo-rotation (about —80°), whereas African copaiba oil is dextro-rotatory. Gurjun oil may be detected by the following colour test: Add 5 drops of the oil to 10 cc. of glacial acetic acid containing 5 drops of nitric acid. A violet colour is developed in a minute or so if gurjun oil is present. Any slight colour developing after this time should be disregarded. When fractionally distilled *in vacuo*, collecting the distillate in fractions of 10 per cent., each fraction should be lævo-rotatory. The B.P. states that the first 10 per cent. should have an optical rotation lower than the oil itself. This is not invariably the case with genuine oils.[1]

Coriander Oil.—A colourless or pale yellow oil, distilled from *Coriandrum*

[1] For the more complete examination of the oil and the conclusions to be drawn from the results of fractionation, see Evans, *Analytical Notes*, 1912, p. 26, or Parry, *Essential Oils*, ii. 453.

sativum. Chief constituent, *dextro*-linalol, 65 to 70 per cent. *Characteristics:* S.G. 0·870 to 0·885; refractive index, 1·457 to 1·478; optical rotation, +8° to +14°; solubility in 70 per cent. alcohol, 1 in 3.

Cubebs Oil.—A colourless or greenish-yellow oil distilled from the fruits of *Piper cubeba*. *Characteristics:* S.G. 0·910 to 0·930; refractive index, 1·490 to 1·500; optical rotation, −25° to −40°; solubility in 90 per cent. alcohol, 1 in 1 to 10. From 65 to 80 per cent. distils between 250° and 280° C. (the B.P. requires not less than 60 per cent.). The oil of "false cubebs,"[1] which is sometimes mixed with genuine cubebs, is entirely different in its characteristics, having S.G. about 0·894; optical rotation, +16° The greater proportion distils below 250° C.

Dill Oil (*Oleum Anethi*, B.P.).—A colourless or pale yellow oil, distilled from the fruit of *Anethum graveolens*. Chief constituent, carvone. *Characteristics:* S.G. 0·900 to 0·920; refractive index, 1·483 to 1·489; optical rotation, +70° to +80°; carvone content, 30 to 60 per cent.; solubility in 90 per cent. alcohol, 1 in 3. The carvone is determined by the neutral sulphite process (p. 310). Not more than 15 per cent. should distil below 15° C., and not less than 40 per cent. above 220° C.

Eucalyptus Oil.—The number of species of eucalyptus is very large, and the oils obtained from them differ very widely. Eucalyptus oil, B.P., is obtained from several species. The B.P. states that it is distilled from the fresh leaves of *Eucalyptus globulus*, *E. dumosa*, and other species of eucalyptus. Very little is now obtained from the two first named, the chief species used being *E. polybractea*, *E. Smithii*, and *E. Australiana*. The chief constituent of these oils and that by which they are valued is cineol or eucalyptol. *B.P. Characteristics*: S.G. 0·910 to 0·930; optical rotation, −10° to +10°; solubility in 70 per cent. alcohol, 1 in 5; cineol content, not less than 55 per cent. by volume. The refractive index of B.P. oils lies between 1·460 and 1·466. The B.P. gives a test for phellandrene in order to exclude oils containing a large proportion of that constituent. 1 cc. of oil is mixed with 2 cc. of glacial acetic acid and 5 cc. of petroleum ether; 2 cc. of a saturated solution of sodium nitrite is then added, and the mixture gently shaken; no crystalline precipitate should form in the upper layer.

Determination of Cineol.—Phosphoric Acid Process.—The official method for the determination of cineol is by the use of phosphoric acid, which forms a crystalline compound with cineol. It is best carried out as follows: 10 cc. of the oil in a dish surrounded by ice are mixed with about an equal volume of phosphoric acid (S.G. 1·75), which is added drop by drop with constant stirring. When sufficient phosphoric acid has been added, a red colour is produced and the mass becomes more liquid. The crystalline mass is then pressed several times between calico surrounded by blotting paper, breaking up the cake between each pressing until it powders easily. The cake is then broken up and transferred to a funnel in the neck of a cassia flask, into which it is washed with boiling water. The flask is heated on the water bath for fifteen minutes, cooled, and water added to bring the cineol into the neck, where it is measured. The cineol so obtained should freeze on cooling to −3° C. There is much difference of opinion with regard to the phosphoric acid process; undoubtedly if not carefully carried out it will give varying results, and the results in the hands

[1] Umney and Potter, *Perf. & Ess. Oil Rec.*, 1912, 3, 64.

of different chemists often differ widely. The method has been to a large extent superseded by the process which is now to be described:

Cresineol Process.[1]—Weigh out 3 gm. of the oil in a tared test-tube, and add 2·1 gm. of pure ortho-cresol. Warm to about 60° C. and place in a bottle fitted with a bored cork, so that the bottle forms an outer jacket. Allow the temperature to fall slowly. When the mass solidifies the temperature suddenly rises. The highest reading is taken, and the percentage of cineol read off from the following table:

Temperature, ° C.	Per cent. Cineol.	Temperature, ° C.	Per cent. Cineol.	Temperature, ° C.	Per cent. Cineol.
55·2	100	46·5	79·2	37·5	62·5
55	99·5	46	78·0	37	61·6
54·5	97·5	45·5	76·7	36·5	61·0
54	96·5	45	75·8	36	60·5
53·5	95	44·5	74·5	35·5	59·7
53	93·7	44	73·7	35	58·8
52·5	92·3	43·5	72·7	34·5	58·0
52	91·2	43	71·7	34	57·0
51·5	90·0	42·5	70·5	33·5	56·7
51	89·0	42	69·6	33	56·2
50·5	87·7	41·5	68·3	32·5	55·5
50	86·8	41	67·5	32	55·0
49·5	85·7	40·5	66·7	31·5	54·5
49	84·5	40	66·0	31	54·0
48·5	83·7	39·5	65·2	30·5	53·5
48	82·7	39	64·8	30	53·0
47·5	81·7	38·5	63·8		
47	80·5	38	63·5		

Fennel Oil (*Ol. Fœniculi*).—The oil distilled from the fruit of *Fœniculum vulgare*. Chief constituent, anethol. *Characteristics:* S.G. 0·964 to 0·995; refractive index, 1·528 to 1·538; optical rotation, +6° to +20°; solidifying point (see Anise Oil, p. 313), +5° to +10° C.; solubility in 90 per cent. alcohol, 1 in 1. Oils are sometimes met with from which the anethol has been removed, with a consequent lowering of the S.G. and solidifying point.

Juniper Berry Oil.—The oil distilled from the ripe fruit of *Juniperus communis*. *Characteristics:* S.G. 0·862 to 0·890; refractive index, 1·474 to 1·490; optical rotation, —3° to —15°; solubility in 95 per cent. alcohol, 1 in 4 (when freshly distilled). The above are the limits given in the B.P., but the oil alters considerably with age, and the above apply to a moderately fresh oil. The S.G. and refractive index gradually increase on keeping.

Lavender Oil.—A pale yellow oil distilled from the flowers of *Lavandula vera*. English lavender oil is more highly valued than the foreign oil, from which it differs in odour and especially in ester content. Important constituent, linalyl acetate. *Characteristics:* S.G. 0·883 to 0·900; refractive index, 1·460 to 1·466; optical rotation, —3° to —10°; solubility in 70

[1] Cocking, *Perf. & Ess. Oil Rec.*, 1920, **11**, 362; *Y.B.P.*, 1920, 395.

per cent. alcohol, 1 in 4. English oils contain from 7 to 11 per cent. of linalyl acetate, and foreign oils 28 to 60 per cent. Lavender oil is subject to adulteration with spike lavender oil, which lowers the ester value and rotation, but more often with artificial esters, for which the various methods of test given on p. 311 may be employed. Occasionally both are used. Spike lavender oil contains about 30 per cent. of free alcohols, whereas lavender oil contains only small amounts.

Lemon Oil.—Lemon oil is a pale yellow oil obtained from lemon peel. It consists mainly of terpenes, but its chief odorous constituent is the aldehyde citral. *Characteristics:* B.P. limits, S.G. 0·857 to 0·860; refractive index, 1·475 to 1·478; optical rotation, +58° to +64°; citral content, not less than 4 per cent. (usual range 4 to 5·5 per cent.). Occasionally genuine oils are met with the characteristics of which lie outside these limits. The characteristics, particularly the citral content and the optical rotation, vary somewhat from year to year—*e.g.* one year's oil may be higher than the average in citral content, whereas the next year's may be distinctly lower.

Determination of Citral. (Hydroxylamine Method.)—The citral is best determined by the hydroxylamine method, which is carried out as follows: To 20 gm. of lemon oil, weighed in a flask which is fitted by a ground joint to a reflux condenser, add 20 cc. of a 5 per cent. solution of hydroxylamine hydrochloride in 80 per cent. alcohol (rectified spirit should be used), 8 cc. of N alcoholic potash solution, and 20 cc. of 90 per cent. alcohol. Attach the flask to the condenser and boil for thirty minutes. It is important that the oil should be in solution when the liquid boils. If this is not the case a little more 90 per cent. alcohol should be added. Wash down the condenser with water, and transfer the contents of the flask with 250 cc. of water to a large conical flask. Titrate the liquid with N alcoholic potash to phenolphthalein until a pink colour is produced. A blank experiment is carried out in the same way, omitting the oil. It is advisable to carry out the final titration until the shade of colour is the same in each case, as the end-point is somewhat difficult to see. The difference between the two titrations with acid $\times 0{\cdot}38$=percentage of citral in the oil. 1 cc. $N/2$ HCl $\equiv$ 0·076 gm. citral.

The following method has been recommended by Bennett and Salamon [1] for the determination of citral:

Solutions Required.—Hydroxylamine hydrochloride solution: Dissolve 5 gm. of hydroxylamine hydrochloride in 9 cc. of hot water, add 80 cc. of 90 per cent. alcohol, 2 cc. of bromophenol blue solution, and neutralise, if necessary, with $N/2$ alcoholic soda. Make up to 100 cc. with 90 per cent. alcohol. Bromophenol blue solution: grind 0·1 gm. of the indicator with 3 cc. of $N/20$ soda, and make up to 25 cc. with water.

Method.—Pipette 10 cc. of lemon oil into a flask, and add 20 cc. of the hydroxylamine solution. Run in $N/2$ alcoholic soda drop by drop with constant shaking until a permanent green colour is obtained. Percentage

$$\text{citral} = \frac{100 \times 0{\cdot}076 \times \text{cc. } N/2 \text{ NaOH used}}{8{\cdot}5}.$$

The usual adulterants of lemon oil are lemon or orange terpenes obtained in the manufacture of "terpeneless" lemon oil, or oils poor in citral. Citral obtained from lemongrass oil may be added to bring up the citral content.

[1] *Analyst*, 1927, 52, 693.

Turpentine may also be used alone or in combination with orange terpenes. The first 10 per cent. of distillate obtained when lemon oil is distilled from a three-bulb fractionating flask should have an optical rotation lower than the original oil by not more than 5°. The presence of turpentine would considerably increase this difference. Further examination should proceed on the lines of careful fractionation, and a comparison of the characteristics of the fractions obtained with those obtained from pure oils.

Lemongrass Oil (*Ol. Graminis Citrati*).—This oil is distilled from lemon grass, *Cymbopogon citratus* and *C. flexuosus*. It is sometimes erroneously called Oil of Verbena, to which its odour is similar. Chief constituent, citral. *Characteristics:* S.G. 0·880 to 0·905; refractive index, 1·482 to 1·488; optical rotation, −3° to +3°; citral content (by bisulphite process), 68 to 85 per cent. The neutral sulphite method, which is official in the B.P., gives results from 3 to 6 per cent. lower than the bisulphite method.

Mustard Oil, Essential (*Ol. Sinapis Volatile*).—Mustard oil is distilled from mustard seeds which have been macerated in water in order that the enzyme myrosin which occurs in the seeds may act upon the potassium myronate, which is also present, with the formation of allyl isothiocyanate, which is the chief constituent of the oil. Mustard oil is a colourless or pale yellow oil, and is a powerful vesicant. *Characteristics:* S.G. 1·014 to 1·025; refractive index, 1·526 to 1·530; optical rotation, nil; boiling range, 148° to 155° C.; allyl isothiocyanate content, about 94 per cent.

Determination of Allyl Isothiocyanate.—1 gm. of the oil is weighed into a flask and made up to 50 cc. with 90 per cent. alcohol. 5 cc. of this solution are mixed in a 100 cc. flask with 50 cc. of $N/10$ silver nitrate and 10 cc. of ammonia solution. The flask is allowed to stand in the dark for twenty-four hours with occasional shaking, heated in a water bath at 80° C. for thirty minutes, cooled to 15·5° C., made up to 100 cc. with water, and filtered. 50 cc. of the filtrate are titrated with $N/10$ thiocyanate after adding 6 cc. of dil. nitric acid and 2 cc. of iron alum solution. 1 cc. of $N/10$ silver nitrate ≡ 0·004957 gm. allyl isothiocyanate.

Nutmeg Oil (*Ol. Myristicæ*).—A pale yellow oil distilled from the fruits of *Myristica fragrans*. *Characteristics:* S.G. 0·868 to 0·922; refractive index, 1·476 to 1·486; optical rotation, +11° to +30°; solubility in 90 per cent. alcohol, 1 in 3. A small amount of fixed oil of nutmeg is usually present, but the residue obtained on heating 2 gm. of the oil for twelve hours on the water bath in a flat dish should not be more than 5 per cent., and is usually not more than 2 per cent.

Pennyroyal Oil (*Ol. Menthæ Pulegii*).—The oil distilled from the pennyroyal herb, *Mentha pulegium*. Chief constituent, pulegone. *Characteristics:* S.G. 0·930 to 0·955; refractive index, 1·482 to 1·487; optical rotation, +15° to +25°; solubility in 70 per cent. alcohol, 1 in 3; pulegone content, not less than 80 per cent. Pulegone is determined by the neutral sulphite method (see p. 310).

Peppermint Oil (*Ol. Menthæ Piperitæ*).—Peppermint oil is distilled from the herb *Mentha piperita*, or in the case of Japanese oils from *Mentha arvensis*. The B.P. oil must be distilled from *Mentha piperita*. The three chief varieties of peppermint oil are English, American, and Japanese; a certain amount is distilled in France and other countries. The first is the most highly valued. It is distilled from two varieties of *Mentha piperita*, the "black" and the "white" mints, the latter of which has the

finer odour. The Japanese oil is inferior in odour, and is chiefly used for the manufacture of menthol; it can, however, be refined to produce an oil of good quality. Most of the oil arriving in this country has been dementholised to a greater or less extent. Chief constituent, menthol, with varying proportions of menthyl acetate and menthone. Table of characteristics:—

	English.	American.	Japanese [1] (dementholised).
Specific gravity .	0·900 to 0·910	0·900 to 0·915	0·898 to 0·908
Refractive index .	1·460 to 1·465	1·460 to 1·471	1·460 to 1·464
Optical rotation .	—24° to —36°	—18° to —35°	—26° to —35°
Total menthol .	55 to 68 per cent.	50 to 62 per cent.	45 to 60 per cent.
Combined menthol	4 to 14 ,,	5 to 14 ,,	5 to 12 ,,
Solubility in 70 per cent. alcohol .	1 in 4	1 in 4	1 in 3

The following standards are given by the B.P.: S.G. 0·900 to 0·920; optical rotation, —20° to —35°; solubility in 70 per cent. alcohol, 1 in 4; total menthol, not less than 50 per cent.; menthyl acetate, not less than 5 per cent.

Pimento Oil.—The oil distilled from the fruit of *Pimenta officinalis*. Chief constituent, eugenol. *Characteristics:* S.G. 1·030 to 1·056; refractive index, 1·528 to 1·535; optical rotation, —0·5° to —5°; phenols, 65 to 82 per cent.; solubility in 70 per cent. alcohol, 1 in 2.

Pine Oil, Siberian (Oil of Siberian Fir, *Ol. Abietis*, B.P.).—Chief constituent, bornyl acetate. S.G. 0·900 to 0·920; refractive index, 1·467 to 1·476; optical rotation, —30° to —43°; esters as bornyl acetate, 30 to 40 per cent.; soluble in 1 volume of 90 per cent. alcohol.

Pinus Pumilio Oil.—The oil distilled from the mountain or dwarf pine, *Pinus pumilio*. S.G. 0·863 to 0·876; refractive index, 1·474 to 1·480; optical rotation, —5° to —15°; esters (as bornyl acetate), 3 to 10 per cent.; soluble in 5 to 10 vols. of 90 per cent. alcohol. Not more than 1 per cent. should distil below 165° C.

Pine Oil, American (Spruce-needle Oil, *Ol. Abietis Canadensis*).—S.G. 0·902 to 0·923; refractive index, 1·469 to 1·471; optical rotation, —14° to —22°; esters (as bornyl acetate), 36 to 52 per cent.

Rose Oil.—Otto of rose is distilled in many countries, but chiefly in Bulgaria and France, from several varieties of rose. The chemical and physical characteristics of the oil vary with the country or district of production, with the variety of rose used, and with the season. It is therefore very difficult to lay down standards for this oil, and the figures given must be interpreted with caution. The otto of rose of Bulgaria, distilled chiefly from *Rosa damascena*, is the finest in odour and the most valuable. The chief constituents of otto of rose are the alcohols geraniol and citronellol, and the "stearoptene," which is a mixture of hydrocarbons, solid

[1] Occasionally oils are met with which are completely dementholised. These have a lower S.G. and higher optical rotation and are insoluble in 70 per cent. alcohol.

at the ordinary temperature, and the cause of the semi-solid nature of the otto. The stearoptene has no odour value. *Characteristics:* The best qualities of Bulgarian rose oil usually lie within the following limits; S.G. 30°/15·5° C., 0·849 to 0·858; refractive index at 25° C., 1·458 to 1·465; optical rotation, −1·5° to −4°; M.Pt., 19° to 22° C.; total alcohols (as geraniol), 68 to 78 per cent.; citronellol, 28 to 34 per cent.; ester value, 8 to 16. On account of the semi-solid nature of the oil the physical constants must be determined above the M.Pt.

Determination of Citronellol by Formylation.—10 cc. of the oil are treated with 20 cc. of formic acid (S.G. 1·226), and boiled for an hour in an acetylation flask under a reflux condenser. 100 cc. of water are then added, and the oily layer washed with water in a separator until the washings are neutral. The formylated oil is dried over anhydrous sodium sulphate, filtered, and the saponification value determined as in the acetylation process. $\text{Citronellol} = \frac{0{\cdot}156 \times 100x}{w - (0{\cdot}028x)}$, where x=number of cc. N alcoholic potash absorbed, and w=weight of formylated oil.

Otto of rose is subject to many and various forms of adulteration, many of them of such an ingenious nature as to defy detection. Geraniol, citronellol, artificial esters, guaiacum wood oil, gurjun balsam oil (for detection, see p. 315), and alcohol are among the adulterants, whilst spermaceti, stearin, or paraffin wax may be added to bring the M.Pt. up to a normal value. Artificial esters, spermaceti, or stearin may be detected by an increase in the ester value and by the separation of the fatty acids. Alcohol may be detected by the increase in the refractive index of the oil after washing with water; the difference in the case of genuine oils is not greater than 0·001.

Rosemary Oil.—Rosemary oil (*Ol. Rosmarini*, B.P.) is a pale yellow oil distilled from the flowering tops of *Rosmarinus officinalis*. The chief varieties are French, Dalmatian or Italian, and Spanish, but some is distilled in England. Important constituents are borneol and camphor, with a small amount of bornyl acetate. *Characteristics:*—

	English.	French.	Spanish.
Specific gravity .	0·895 to 0·905	0·900 to 0·920	0·900 to 0·910
Refractive index .	1·4652 to 1·467	..	1·467 to 1·470
Optical rotation .	−3° to +3°	Up to +13°	−4° to +10°
Esters (as bornyl acetate),	About 5 per cent.	1 to 5 per cent.	1 to 3·5 per cent.
Alcohols (as borneol)	About 14 per cent.	8 to 11 per cent.	10 to 14 per cent.

Rosemary oil is soluble in 90 per cent. alcohol (1 in 1), and in 80 per cent. alcohol (1 in 5 to 10). The above limits will include most normal oils, but occasionally the optical rotation is negative up to −6° or higher.

Rue Oil.—Rue oil is distilled from various species of rue, but chiefly

from *Ruta graveolens*. *Usual characteristics:* S.G. 0·830 to 0·845; refractive index, 1·430 to 1·438; optical rotation, −0·5° to +3°; solidifying point, 5° to 11° C.; solubility in 70 per cent. alcohol, 1 in 3.

Sandalwood Oil.—East Indian sandalwood oil is obtained from the heart wood of *Santalum album*, the chief constituent being santalol. This is the only oil official in the B.P. West Australian sandalwood oil is distilled from *Eucarya spicatus*. It is doubtful whether the alcohol which forms its chief constituent is identical with santalol. The official oil has the following *characteristics:* S.G. 0·973 to 0·985; refractive index, 1·500 to 1·510; optical rotation, −13° to −21°; total alcohols (as santalol), 90 to 97 per cent. The oil should be soluble in 6 vols. of 70 per cent. alcohol at 20° C.[1] West Australian sandalwood oil has the characteristics[2]: S.G. 0·967 to 0·973; refractive index, 1·505 to 1·507; optical rotation, −8° to −15·5°. Total alcohols (as santalol), 90 to 93 per cent.

Sassafras Oil.—Sassafras oil is distilled from the root of *Sassafras officinale*. Chief constituent, safrol. *Characteristics:* S.G. 1·070 to 1·080; refractive index, 1·528 to 1·529; optical rotation, +2° to +5°; solubility in 90 per cent. alcohol, 1 in 2. Sassafras oil is often adulterated with or substituted by artificial safrol from camphor oil. This raises the S.G. and refractive index and lowers the optical rotation of the oil, and it may be recognised by its odour.

Savin Oil.—Savin oil (*Oleum Sabini*) is distilled from the fresh twigs of *Juniperus sabina*. Oil of "false savin," or French savin, is distilled from *Juniperus Phœnicea*, and has very different characteristics. Chief constituent, sabinyl acetate. *Characteristics:*—

	True Savin.	False Savin.
Specific gravity	0·907 to 0·930	0·863 to 0·892
Refractive index	1·472 to 1·480	..
Optical rotation	+36° to +63°	+2° to +8°
Ester value	104 to 135	0 to 26
Solubility in 90 per cent. alcohol	1 in 1	1 in 1

Spearmint Oil.—Spearmint oil is distilled in this country and in the United States chiefly from *Mentha viridis*. Chief constituent, carvone. *Characteristics:* S.G. 0·920 to 0·940; refractive index, 1·480 to 1·489; optical rotation, −35° to −53°; carvone content, 30 to 65 per cent.; solubility in 80 per cent. alcohol, 1 in 1·5. The carvone is determined by the neutral sulphite method (p. 310).

Thyme Oil.—Thyme oil is chiefly distilled from *Thymus vulgaris*. It is found in commerce as the "red" and "white" varieties, the former being the crude variety, having a red colour, probably due to iron, and the latter being the rectified, almost colourless oil. Thyme oil is subject to adulteration with turpentine or to admixture with oil from other species of thyme. Chief constituents, thymol and carvacrol. Thymol is found in the larger

[1] See also Parry, *C. & D.*, 1927, **107**, 710.
[2] May, *C. & D.*, 1928, **108**, 42.

proportion in French oils, while Spanish oils, which are inferior to the French oils, contain a larger amount of carvacrol. *Characteristics* :—

	French.	Spanish.
Specific gravity	0·905 to 0·935	0·928 to 0·958
Refractive index . .	1·480 to 1·495	1·502 to 1·511
Optical rotation . . .	—0·5° to —4°	+2° to —4°
Phenols	20 to 40 per cent.	50 to 75 per cent.
Solubility in 80 per cent. alcohol	1 in 2	..
Solubility in 70 per cent. alcohol	..	1 in 3

The addition of turpentine reduces the solubility, the phenol content, and the S.G. Oil of *Thymus serpyllum* increases the lævo-rotation, but does not alter the S.G.

Turpentine Oil (Oil of Turpentine, *Oleum Terebinthinæ Rectificatum*) is officially described as distilled from the oleo-resin, turpentine, obtained from various species of *Pinus*, and rectified. Much turpentine, however, is not produced in this way, but is directly distilled from pine wood, and is known as "wood turpentine." The bulk of the supplies of oil of turpentine are obtained from America, but considerable quantities are distilled in France, Russia, and elsewhere. *Characteristics* :—

	American.	French.
Specific gravity	0·862 to 0·870	0·863 to 0·875
Refractive index . . .	1·468 to 1·473	1·468 to 1·475
Optical rotation . . .	Variable	—20° to —38°

American gum turpentine begins to boil at about 155° C., and 95 per cent. should distil below 170° C. Turpentine is liable to be adulterated with "wood turpentine" or "petroleum turpentine." The former, if carefully fractionated, may be difficult to detect, but petroleum spirit will lower the S.G. and refractive index, and considerably affect the temperature of distillation.

Wintergreen Oil (Oil of Wintergreen, *Oleum Gaultheriæ*, B.P.) may be distilled either from the leaves of *Gaultheria procumbens* or from the bark of *Betula lenta*; usually commercial oils are from the latter. In either case the oil consists almost entirely of methyl salicylate. *Characteristics:* S.G. 1·180 to 1·189; refractive index, 1·536 to 1·538; optical rotation, 0° to —1°; solubility in 70 per cent. alcohol, 1 in 6; esters (as methyl salicylate), not less than 99 per cent. B.P. Wintergreen oil often contains or is substituted by artificial methyl salicylate (*q.v.*, p. 157). The following colour test [1] sometimes affords useful information as to whether an oil consists of pure artificial methyl salicylate or not. Mix in a test-tube

[1] Umney, *Perf. & Ess. Oil Rec.*, 1914, 60.

5 drops of the oil, 5 drops of a 5 per cent. alcoholic solution of vanillin, and 1 cc. of alcohol. Shake well, and add 2 cc. of conc. sulphuric acid; mix. Gaultheria oil gives a crimson colour, betula oil a blood-red colour, but artificial methyl salicylate gives a yellow colour.

Wormseed Oil (Oil of Wormseed, *Oleum Chenopodii*) is distilled from the herb *Chenopodium ambrosoides*. *Characteristics:* S.G. 0·958 to 0·990; refractive index, 1·474 to 1·480; optical rotation, —4° to —12°; solubility in 70 per cent. alcohol, 1 in 3 to 10. No distillation should take place below 170° C.

Determination of Ascaridol.—Shake 10 cc. of the oil in an absorption flask with 60 v/v acetic acid. Make up to the mark with the acetic acid, and allow to stand. The volume absorbed is calculated as ascaridol.

APPENDIX.

ABBREVIATIONS OF JOURNALS.

Amer. J. Pharm. .	*American Journal of Pharmacy*, 148 North Tenth Street, Philadelphia, Pa., U.S.A.
Analyst . . .	*Analyst*, 4 Petty Cury, Cambridge.
Annal. Chim. Appl. .	*Annali di Chimica Applicata.* Via Quattro Novembre 154, Rome, Italy.
Apoth. Ztg. . .	*Apotheker Zeitung.* Levetos owstrasse 166, Berlin, N.W.
Ber.	*Berichte der Deutschen Chemischen.* Gesellschaft-Verlag Chemie, Leipzig, Germany.
Biochem. J. . .	*Biochemical Journal*, Cambridge University Press, Fetter Lane, E.C. 4.
Boll. Chim. farm. .	*Bollentino Chimico-Farmaceutico.* Via Cappuccio 19, Milan, Italy.
Chem. Abs. . .	*Chemical Abstracts.* Published by American Chemical Society, Mills Buildings, Washington, D.C., U.S.A.
C. & D. . . .	*Chemist and Druggist*, 42 Cannon Street, London, E.C.
Compt. rend. . .	*Comptes-Rendus hebdomadaires des Séances de l'Académie des Sciences*, Quai des Grands-Augustins 55, Paris.
Ind. Eng. Chem. . .	*Journal of Industrial and Engineering Chemistry*, Mills Buildings, Washington, D.C., U.S.A.
J. Amer. Chem. Soc. .	*Journal of the American Chemical Society*, Mills Buildings, Washington, D.C., U.S.A.
J. Ass. Off. Agr. Chem.	*Journal of the Association of Official Agricultural Chemists*, Box 290, Pennsylvania Avenue Station, Washington, D.C., U.S.A.
J. Biol. Chem. . .	*Journal of Biological Chemistry*, Rockefeller Institute, Baltimore, Md., U.S.A.
J. Pharm. Chim. .	*Journal de Pharmacie et de Chimie*, Place de l'Odéon 8, Paris.
J. Soc. Chem. Ind. .	*Journal of the Society of Chemical Industry*, Central House, Finsbury Square, E.C. 2.
Perf. & Ess. Oil Rec. .	*Perfumery and Essential Oil Record*, 6 Serle Street, W.C.
Pharm. J. . . .	*Pharmaceutical Journal*, 17 Bloomsbury Square, W.C. 1.
Pharm. Weekblad .	*Pharmaceutische Weekblad*, O.Z. Voorburgwal 115, Amsterdam.
Pharm. Zeit. . .	*Pharmazeutische Zeitung*, Linkstrasse 23, Berlin, W. 9.
Y.B.P. . . .	*Year Book of Pharmacy*, 17 Bloomsbury Square, W.C. 1.
Z. Anal. Chem. . .	*Zeitschrift fur analytische Chemie.*
Z. Angew. Chem. .	*Zeitschrift fur angewandte Chemie.*

LIST OF GENERAL ABBREVIATIONS.

S.G. . . .	Specific gravity $\frac{15\cdot5° C.}{15\cdot5° C.}$
M.W.. . .	Molecular weight.
B.P. . . .	British Pharmacopœia (1914 edition).
U.S.P. . .	United States Pharmacopœia (10th edition).
P.G. . . .	German Pharmacopœia (6th edition).
$[\alpha]_D$ . . .	Specific rotation for the sodium line.
A.R. . . .	Analytical reagent chemicals.
v/v . . .	Cc. per 100 cc.
w/v . . .	Gm. per 100 cc.
T.S. . . .	Total solids.

PREPARATION OF STANDARD SOLUTIONS.

One litre of decinormal solution contains the following weight in gm. :—

Ammonium thiocyanate .	7·612
Hydrochloric acid . .	3·647
Iodine	12·693
Oxalic acid	6·302
Potassium bichromate . .	4·903
„ bromide-bromate .	2·784 potassium bromate and 15 gm. potassium bromide.
„ hydroxide . .	5·611
„ permanganate .	3·161
„ thiocyanate . .	9·718
Silver nitrate . . .	16·989
Sodium carbonate. . .	5·300
„ hydroxide . .	2·000
„ thiosulphate . .	24·820
Sulphuric acid . . .	4·904

LIST OF BOOKS SUITABLE FOR THE MICROSCOPICAL ANALYSIS OF DRUGS.

A Compendium of Food-Microscopy, E. G. Clayton. London: Baillière, Tindall, & Cox.

The Microscopical Examination of Foods and Drugs, H. G. Greenish. London: J. & A. Churchill.

An Anatomical Atlas of Vegetable Powders, Greenish and Collin. London: J. & A. Churchill.

Pharmakognostischer Atlas, J. Moeller. Berlin.

Microscopy of Vegetable Foods, A. L. Winton. London: Chapman & Hall.

THE STANDARDISATION OF ACID AND ALKALI.

Of the many methods available the following will be found convenient, accurate, and reliable.

Where large quantities are likely to be required it is well to prepare normal hydrochloric acid in a bottle of some 8 to 10 litres capacity. This is made up

approximately by assuming that the laboratory pure strong acid is ten times normal. The strength of the approximately normal acid is then accurately determined by means of pure sodium carbonate. The purest anhydrous sodium carbonate obtainable is heated in thin layers in an air-oven at about 150° C. for at least two hours. It is then allowed to cool in a stoppered bottle in the desiccator. 5·3000 gm. of the dried sodium carbonate are accurately weighed out and washed into a convenient vessel. 100 cc. of the roughly normal acid are then added from a standard 100 cc. pipette (taking the usual precautions with regard to temperature of liquid and draining of pipette), the vessel being inclined and covered with a watch-glass while the action is taking place. When the action has ceased, the liquid is brought to the boil, methyl red solution added, and the titration completed with $N/10$ acid or alkali as the case may be. From the result so obtained the stock solution of roughly normal acid is adjusted as nearly as possible to normal, and the titration repeated. At the second titration the solution should be nearly correct; its strength should be adjusted until only two or three drops of $N/10$ acid or alkali are necessary to adjust the 100 cc. The boiling should be continued until it is quite certain that all carbon dioxide has been evolved.

Decinormal hydrochloric acid may be prepared by filling a standard litre flask with water at 15° C. and removing 110 cc. (This is to make it possible for the pipette to be drained by touching the surface of the liquid in the flask.) 100 cc. of the normal acid (at 15° C.) are then run in from a standard pipette, the whole well shaken and diluted accurately to the mark.

Decinormal sodium hydroxide solution may be prepared by diluting a clear, 50 per cent. A.R. sodium hydroxide solution until it is about $N/10$ strength and then adjusting by means of the $N/10$ hydrochloric acid. Different indicators will not give quite the same reading and the solution should be adjusted with that indicator with which the solution is to be used subsequently.

The decinormal sodium hydroxide may be checked by weighing out the requisite quantities of pure oxalic acid or potassium hydrogen phthalate and titrating.

For standard acid, pure guanidine carbonate may be used (1 cc. $N/10$ acid $\equiv$0·0090072 gm.), but the readings so obtained do not quite agree with those from sodium carbonate, which are usually accepted as being more accurate.

PREPARATION OF REAGENTS.

Alumina Cream.—A cold saturated solution of alum is precipitated with slight excess of ammonia. More saturated alum solution is then added to the mixture until slightly acid. The precipitated alumina is washed by decantation until soluble material is removed.

Ammoniacal Silver Nitrate Solution.—2·5 gm. of silver nitrate are dissolved in about 80 cc. of water and 10 per cent. ammonia added until the precipitate formed is nearly redissolved. The solution is allowed to stand, decanted and diluted to 100 cc.

Ammonium Carbonate Solution.—50 gm. of ammonium carbonate are dissolved in water, 75 cc. of 10 per cent. ammonia (S.G. 0·959) added, and the whole diluted to 1 litre.

Ammonium Molybdate Solution.—10 gm. of molybdic acid are dissolved in a mixture of 14 cc. of ammonia (S.G. 0·880) and 28 cc. of water. 125 cc. of a mixture of equal volumes of concentrated nitric acid and water are then run in slowly with continual shaking. If necessary the solution is filtered after standing twenty-four hours.

Baudouin's Reagent.—A 1 per cent. solution of sucrose in concentrated HCl (S.G. 1·20).

Becchi's Reagent.—A 1 per cent. solution of silver nitrate in absolute alcohol is mixed with 20 cc. of ether and 1·5 cc. of $N/2$ nitric acid.

Calcium Hypochlorite Solution.—100 gm. of bleaching powder are triturated with water and the solution made up to one litre, allowed to stand, and the clear solution decanted.

Copper Ammonium Sulphate Solution.—5 gm. of copper sulphate are dissolved in 75 cc. of water and 10 per cent. ammonia cautiously added until the precipitate is nearly redissolved. The solution is then filtered and diluted to 100 cc.

Dragendorff's Reagent.—8 gm. of bismuth nitrate are dissolved in 20 cc. of nitric acid (S.G. 1·15) and the solution mixed with a solution of 27 gm. of potassium iodide in 40 cc. of water. After standing some time the clear liquid is decanted from the deposited crystals and diluted to 100 cc.

Fehling's Solution.—The copper solution should contain 69·278 gm. of crystallised copper sulphate solution per litre; the alkaline solution 346 gm. of Rochelle salt and 130 gm. of sodium hydroxide per litre.

Ferric Iron Indicator.—5 gm. of iron alum are dissolved in 50 cc. of water, 50 cc. of concentrated nitric acid added, and the solution boiled until oxides of nitrogen are expelled.

Frohde's Reagent.—0·01 gm. of sodium molybdate is dissolved in 1 cc. of concentrated sulphuric acid by gently warming.

Griess-Ilosvay Reagent.—0·1 gm. of α-naphthylamine is heated with 20 cc. of glacial acetic acid and the solution mixed with 280 cc. of roughly normal acetic acid containing 0·5 gm. of sulphanilic acid.

Halphen's Reagent.—A 1 per cent. solution of sulphur in carbon disulphide is mixed with an equal volume of amyl alcohol.

Magnesia Mixture.—15 gm. of magnesium chloride and 20 gm. of ammonium chloride are dissolved in 150 cc. of water and mixed with 100 cc. of ammonia (S.G. 0·880). If necessary, the solution is filtered after standing twenty-four hours.

Mandelin's Reagent.—0·01 gm. of sodium vanadate is dissolved in 10 cc. of concentrated sulphuric acid.

Marmé's Reagent.—Prepared by saturating a concentrated boiling solution of potassium iodide with cadmium iodide and then adding an equal bulk of cold saturated solution of potassium iodide.

Mayer's Reagent.—1·35 gm. of mercuric chloride and 5 gm. of potassium iodide are dissolved in 94 cc. of water.

Millon's Reagent.—Metallic mercury is treated with twice its weight of concentrated nitric acid (S.G. 1·42), first in the cold, and, later on, warming until solution is complete. Two volumes of water are added and the whole allowed to stand some hours, when the clear solution is decanted.

Nessler's Reagent.—62·5 gm. of potassium iodide are dissolved in 120 cc. water. A saturated solution of mercuric chloride is poured in until a slight permanent precipitate remains; 220 cc. of a 50 per cent. solution of sodium hydroxide are then added and the whole diluted to one litre. The solution is allowed to stand for some days and the clear liquid decanted.

Phenol Disulphonic Acid.—3 gm. of phenol are heated with 20 cc. of concentrated sulphuric acid on the water bath for six hours.

Potassium Chromate Indicator.—A few drops of silver nitrate solution are added to a 2 per cent. solution of neutral potassium chromate. The solution is filtered.

Schiff's Reagent.—0·2 gm. of magenta base is dissolved in 10 cc. of a freshly prepared, cold, saturated aqueous solution of sulphur dioxide, and after twenty-four hours the solution is diluted to 200 cc. with water.

Sodium Hypochlorite.—150 gm. of crystallised sodium carbonate are dissolved in about 250 cc. of water. 100 gm. of bleaching powder are triturated with water and finally diluted to 750 cc. The two liquids are then mixed, shaken well at first, then occasionally during several hours, and filtered.

Stannous Chloride.—20 gm. of pure metallic tin are gently heated with 60 cc. of concentrated HCl until all action has ceased. The solution is then diluted to 100 cc. and allowed to remain in contact with the undissolved tin.

Wagner's Reagent.—2 gm. of iodine and 5 gm. of potassium iodide in 100 cc. of water.

RELATIONSHIP OF ENGLISH AND METRIC MEASURES.

1 Gram	=15·432 grains.	1 Litre	=35·196 fluid ounces.
1 Kilogram	=15432·35 grains.	1 Millilitre	=16·9 minims.
	=35·274 ounces.	1 Minim	=0·0592 ml.
	=2·2046 pounds.	1 Fluid Ounce	=28·4123 mls.
1 Grain	=0·0648 gm.	1 Centimetre	=0·39370 in.
1 Ounce	=28·350 gm.	1 Metre	=39·370 in.
1 Pound	=453·59 gm.	1 Inch	=25·3999 mm.

SPECIFIC GRAVITY OF ALCOHOL SOLUTIONS.

Specific Gravity in Air at 15·6° C./15·6° C.	Percentage of Ethyl Alcohol.		Specific Gravity in Air at 15·6° C./15·6° C.	Percentage of Ethyl Alcohol.	
	By Weight.	By Volume at 60° F. or 15·6° C.		By Weight.	By Volume at 60° F. or 15·6° C.
0·7940	99·87	99·92	0·8300	87·11	91·11
0·7950	99·55	99·72	0·8310	86·73	90·82
0·7960	99 22	99·52	0·8320	86·34	90·52
0·7970	98·90	99·32	0·8330	85·95	90·22
0·7980	98·57	99·12	0·8340	85·56	89·91
0·7990	98·24	98·91	0·8350	85·17	89·61
0·8000	97·91	98·70	0·8360	84·78	89·30
0·8010	97·59	98·49	0·8370	84·39	88·99
0·8020	97·25	98·28	0·8380	83·99	88·68
0·8030	96·91	98·06	0·8390	83·60	88·37
0·8040	96·57	97·84	0·8400	83·20	88·06
0·8050	96·23	97·62	0·8410	82·80	87·74
0·8060	95·89	97·39	0·8420	82·40	87·42
0·8070	95·55	97·16	0·8430	82·00	87·09
0 8080	95·20	96·93	0·8440	81·60	86·77
0·8090	94·85	96·69	0·8450	81·20	86·44
0·8100	94·50	96·45	0·8460	80·79	86·12
0·8110	94·15	96·21	0·8470	80·39	85·80
0·8120	93·80	95·97	0·8480	79·98	85·46
0·8130	93·44	95·72	0 8490	79·58	85·12
0·8140	93·08	95·47	0·8500	79·17	84·78
0·8150	92·72	95·22	0·8510	78·76	84·44
0·8160	92·36	94·97	0·8520	78·35	84·11
0·8170	92·00	94·71	0·8530	77·94	83·77
0·8180	91·63	94·45	0·8540	77·53	83·42
0·8190	91·27	94·19	0·8550	77·12	83·08
0·8200	90·90	93·92	0·8560	76·71	82·73
0·8210	90·53	93·65	0·8570	76 30	82·38
0·8220	90·16	93·38	0·8580	75·88	82·03
0·8230	89·79	93·11	0·8590	75·47	81·68
0 8240	89·41	92·83	0·8600	75·05	81·32
0·8250	89 03	92·55	0·8610	74·64	80·97
0·8260	88·65	92·26	0·8620	74·22	80·61
0·8270	88·27	91·98	0·8630	73 81	80·25
0·8280	87·88	91·69	0·8640	73·39	79·89
0·8290	87·50	91·40	0·8650	72·97	79·53

SPECIFIC GRAVITY OF ALCOHOL SOLUTIONS.—*Continued.*

Specific Gravity in Air at 15·6° C./15·6° C.	Percentage of Ethyl Alcohol.		Specific Gravity in Air at 15·6° C./15·6° C.	Percentage of Ethyl Alcohol.	
	By Weight.	By Volume at 60° F. or 15·6° C.		By Weight.	By Volume at 60° F. or 15·6° C.
0·8660	72·55	79·16	0·9150	51·43	59·29
0·8670	72·14	78·80	0·9160	50·98	58·83
0·8680	71·72	78·43	0·9170	50·53	58·38
0·8690	71·30	78·06	0·9180	50·08	57·92
0·8700	70·88	77·69	0·9190	49·63	57·46
0·8710	70·46	77·32	0·9200	49·17	56·99
0·8720	70·04	76·94	0·9210	48·71	56·52
0·8730	69·62	76·57	0·9220	48·25	56·05
0·8740	69·19	76·19	0·9230	47·79	55·58
0·8750	68·77	75·82	0·9240	47·33	55·10
0·8760	68·35	75·44	0·9250	46·87	54·62
0·8770	67·93	75·06	0·9260	46·40	54·14
0·8780	67·51	74·68	0·9270	45·94	53·65
0·8790	67·09	74·30	0·9280	45·47	53·16
0·8800	66·66	73·91	0·9290	45·00	52·67
0·8810	66·24	73·52	0·9300	44·53	52·18
0·8820	65·81	73·13	0·9310	44·06	51·68
0·8830	65·39	72·74	0·9320	43·59	51·18
0·8840	64·96	72·34	0·9330	43·11	50·67
0·8850	64·53	71·95	0·9340	42·62	50·15
0·8860	64·10	71·55	0·9350	42·13	49·63
0·8870	63·67	71·15	0·9360	41·64	49·10
0·8880	63·24	70·75	0·9370	41·15	48·57
0·8890	62·81	70·35	0·9380	40·65	48·04
0·8900	62·38	69·95	0·9390	40·15	47·50
0·8910	61·95	69·55	0·9400	39·65	46·95
0·8920	61·52	69·14	0·9410	39·15	46·40
0·8930	61·09	68·74	0·9420	38·64	45·85
0·8940	60·66	68·33	0·9430	38·12	45·28
0·8950	60·23	67·92	0·9440	37·60	44·71
0·8960	59·80	67·50	0·9450	37·07	44·13
0·8970	59·37	67·08	0·9460	36·54	43·54
0·8980	58·93	66·67	0·9470	36·00	42·95
0·8990	58·50	66·25	0·9480	35·46	42·35
0·9000	58·06	65·83	0·9490	34·92	41·74
0·9010	57·62	65·41	0·9500	34·37	41·13
0·9020	57·18	64·98	0·9510	33·81	40·50
0·9030	56·75	64·56	0·9520	33·25	39·87
0·9040	56·31	64·13	0·9530	32·67	39·22
0·9050	55·87	63·70	0·9540	32·09	38·57
0·9060	55·42	63·26	0·9550	31·50	37·89
0·9070	54·98	62·83	0·9560	30·90	37·20
0·9080	54·54	62·39	0·9570	30 28	36·50
0·9090	54·10	61·95	0·9580	29·66	35·79
0·9100	53·65	61·51	0·9590	29·03	35·06
0·9110	53·21	61·07	0·9600	28·39	34·33
0·9120	52·77	60·63	0·9610	27·73	33·56
0·9130	52·33	60·19	0·9620	27·06	32·79
0·9140	51·88	59·74	0·9630	26·37	31·99

SPECIFIC GRAVITY OF ALCOHOL SOLUTIONS.—*Continued.*

Specific Gravity in Air at 15·6° C./15·6° C.	Percentage of Ethyl Alcohol. By Weight.	Percentage of Ethyl Alcohol. By Volume at 60° F. or 15·6° C.	Specific Gravity in Air at 15·6° C./15·6° C.	Percentage of Ethyl Alcohol. By Weight.	Percentage of Ethyl Alcohol. By Volume at 60° F. or 15·6° C.
0·9640	25·68	31·18	0·9820	11·42	14·13
0·9650	24·97	30·34	0·9830	10·65	13·20
0·9660	24·23	29·48	0·9840	9·91	12·29
0·9670	23·48	28·69	0·9850	9·18	11·40
0·9680	22·71	27·69	0·9860	8·46	10·51
0·9690	21·93	26·77	0·9870	7·76	9·65
0·9700	21·14	25·83	0·9880	7·08	8·80
0·9710	20·34	24·85	0·9890	6·41	7·98
0·9720	19·53	23·91	0·9900	5·76	7·18
0·9730	18·72	22·94	0·9910	5·13	6·40
0·9740	17·90	21·96	0·9920	4·51	5·63
0·9750	17·08	20·97	0·9930	3·90	4·88
0 9760	16·25	19·98	0·9940	3·31	4·14
0·9770	15·43	18·99	0·9950	2·73	3·42
0·9780	14·61	18·00	0·9960	2·17	2·71
0·9790	13·80	17·02	0·9970	1·61	2·02
0·9800	12·99	16·04	0·9980	1·07	1·34
0·9810	12·20	15·08	0·9990	0·53	0·66

CORRECTION OF ALCOHOL SPECIFIC GRAVITIES FOR TEMPERATURE.

S.G.	Correction for 1° F.	S.G.	Correction for 1° F.
0·794–0·864	0·00046	0·965–0·966	0·00026
0·864–0·889	0·00045	0·966–0·967	0·00025
0·889–0·902	0·00044	0·967–0·968	0·00024
0·902–0·912	0·00043	0·968–0·969	0·00023
0·912–0·921	0·00042	0·969–0·970	0·00022
0·921–0·928	0·00041	0·970–0·971	0·00021
0·928–0·935	0·00040	0·971–0·972	0·00020
0·935–0·940	0·00039	0·972–0·974	0·00019
0·940–0·943	0·00038	0·974–0·975	0·00018
0·943–0·946	0·00037	0·975–0·976	0·00017
0·946–0·949	0·00036	0·976–0·977	0·00016
0·949–0·951	0·00035	0·977–0·978	0·00015
0·951–0·953	0·00034	0·978–0·980	0·00014
0·953–0·955	0·00033	0·980–0·981	0·00013
0·955–0·957	0·00032	0·981–0·983	0·00012
0·957–0·959	0·00031	0·983–0·985	0·00011
0·959–0·961	0·00030	0·985–0·987	0·00010
0·961–0·962	0·00029	0·987–0·990	0·00009
0·962–0·963	0·00028	0·990–0·995	0·00008
0·963–0·965	0·00027	0·995–1·000	0·00007

REFRACTION OF ALCOHOL SOLUTIONS ON IMMERSION REFRACTOMETER. *PRISM 1.*

Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.	Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.
14·5	0·08	0·06	19·7	4·10	3·27
14·6	0·16	0·13	19·8	4·17	3·33
14·7	0·25	0·20	19·9	4·25	3·39
14·8	0·34	0·27	20·0	4·32	3·45
14·9	0·43	0·34	20·1	4·39	3·51
15·0	0·52	0·41	20·2	4·47	3·57
15·1	0·60	0·48	20·3	4·54	3·63
15·2	0·69	0·55	20·4	4·61	3·68
15·3	0·77	0·61	20·5	4·68	3·74
15·4	0·85	0·68	20·6	4·75	3·80
15·5	0 94	0·75	20·7	4·83	3·86
15·6	1·03	0·82	20·8	4·90	3·92
15·7	1·12	0·89	20·9	4·97	3·98
15·8	1·21	0·96	21·0	5·04	4·03
15·9	1·28	1·02	21·1	5·11	4·09
16·0	1·36	1·08	21·2	5·19	4·15
16·1	1·44	1·14	21·3	5·26	4·21
16·2	1·51	1·20	21·4	5·33	4·26
16·3	1·59	1·26	21·5	5·40	4·32
16·4	1·66	1·32	21·6	5·47	4·38
16·5	1·74	1·38	21·7	5·54	4·44
16·6	1·81	1·44	21·8	5·61	4·49
16·7	1·89	1·50	21·9	5·69	4·55
16·8	1·96	1·56	22·0	5·76	4·61
16·9	2·04	1·62	22·1	5·83	4·67
17·0	2·11	1·68	22·2	5·90	4·72
17·1	2·19	1·74	22·3	5·97	4·78
17·2	2·26	1·80	22·4	6·05	4·84
17·3	2·34	1·86	22·5	6·12	4·90
17·4	2·41	1·92	22·6	6·19	4·95
17·5	2·49	1·98	22·7	6·26	5·01
17·6	2·56	2·04	22·8	6·33	5·07
17·7	2·62	2·09	22·9	6·40	5·13
17·8	2·70	2·15	23·0	6·47	5·18
17·9	2·77	2·21	23·1	6·54	5·24
18·0	2·85	2·27	23·2	6·61	5·30
18·1	2·92	2·33	23·3	6·68	5·36
18·2	3·00	2·39	23·4	6·75	5·41
18·3	3·07	2·45	23·5	6·83	5·47
18·4	3·15	2·51	23·6	6·90	5·53
18·5	3·22	2·57	23·7	6·97	5·59
18·6	3·30	2·63	23·8	7·04	5·64
18·7	3·37	2·69	23·9	7·11	5·70
18·8	3·45	2·75	24·0	7·18	5·76
18·9	3·52	2·81	24·1	7·25	5·82
19·0	3·59	2·86	24·2	7·32	5·87
19·1	3·66	2·92	24·3	7 39	5·93
19·2	3·73	2·98	24·4	7·46	5·99
19·3	3·81	3·04	24·5	7·53	6·04
19·4	3·88	3·10	24·6	7·60	6·10
19·5	3·96	3·16	24·7	7·67	6·15
19·6	4·03	3·22	24·8	7·74	6·21

REFRACTION OF ALCOHOL SOLUTIONS ON IMMERSION REFRACTOMETER. *PRISM 1.—Continued.*

Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.	Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.
24·9	7·81	6·26	30·3	11·45	9·23
25·0	7·88	6·32	30·4	11·51	9·28
25·1	7·94	6·37	30·5	11·58	9·34
25·2	8·01	6·43	30·6	11·64	9·39
25·3	8·07	6·48	30·7	11·71	9·44
25·4	8·14	6·54	30·8	11·78	9·50
25·5	8·21	6·59	30·9	11·84	9·55
25·6	8·28	6·65	31·0	11·91	9·60
25·7	8·35	6·70	31·1	11·97	9·66
25·8	8·42	6·76	31·2	12·04	9·71
25·9	8·48	6·81	31·3	12·11	9·76
26·0	8·55	6·87	31·4	12·17	9·82
26·1	8·62	6·92	31·5	12·24	9·87
26·2	8·69	6·98	31·6	12·30	9·92
26·3	8·75	7·03	31·7	12·37	9·98
26·4	8·82	7·09	31·8	12·43	10·03
26·5	8·89	7·15	31·9	12·50	10·09
26·6	8·96	7·20	32·0	12·57	10·14
26·7	9·03	7·26	32·1	12·63	10·19
26·8	9·10	7·31	32·2	12·70	10·25
26·9	9·17	7·37	32·3	12·76	10·30
27·0	9·23	7·42	32·4	12·83	10·35
27·1	9·30	7·48	32·5	12·89	10·41
27·2	9·37	7·54	32·6	12·96	10·46
27·3	9·44	7·59	32·7	13·03	10·52
27·4	9·51	7·65	32·8	13·09	10·57
27·5	9·58	7·70	32·9	13·15	10·62
27·6	9·65	7·76	33·0	13·22	10·68
27·7	9·72	7·82	33·1	13·28	10·73
27·8	9·79	7·87	33·2	13·35	10·79
27·9	9·86	7·93	33·3	13·41	10·84
28·0	9·92	7·98	33·4	13·48	10·89
28·1	9·99	8·04	33·5	13·54	10·95
28·2	10·06	8·09	33·6	13·61	11·00
28·3	10·13	8·15	33·7	13·67	11·05
28·4	10·19	8·20	33·8	13·74	11·10
28·5	10·26	8·26	33·9	13·80	11·16
28·6	10·32	8·31	34·0	13·86	11·21
28·7	10·39	8·36	34·1	13·93	11·26
28·8	10·46	8·42	34·2	13·99	11·31
28·9	10·52	8·47	34·3	14·06	11·36
29·0	10·59	8·53	34·4	14·12	11·41
29·1	10·66	8·58	34·5	14·18	11·47
29·2	10·73	8·64	34·6	14·25	11·52
29·3	10·79	8·69	34·7	14·31	11·57
29·4	10·86	8·74	34·8	14·37	11·62
29·5	10·93	8·80	34·9	14·43	11·67
29·6	10·99	8·85	35·0	14·50	11·73
29·7	11·06	8·91	35·1	14·56	11·78
29·8	11·12	8·96	35·2	14·62	11·83
29·9	11·19	9·02	35·3	14·69	11·88
30·0	11·26	9·07	35·4	14·75	11·93
30·1	11·32	9·12	35·5	14·81	11·99
30·2	11·38	9·18	35·6	14·87	12·04

REFRACTION OF ALCOHOL SOLUTIONS ON IMMERSION REFRACTOMETER. *PRISM 1.—Continued.*

Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.	Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.
35·7	14·94	12·09	41·1	18·31	14·87
35·8	15·00	12·14	41·2	18·37	14·92
35·9	15·06	12·19	41·3	18·44	14·97
36·0	15·13	12·24	41·4	18·50	15·03
36·1	15·19	12·30	41·5	18·56	15·08
36·2	15·25	12·35	41·6	18·62	15·13
36·3	15·32	12·40	41·7	18·68	15·18
36·4	15·38	12·45	41·8	18·74	15·23
36·5	15·44	12·50	41·9	18·81	15·28
36·6	15·51	12·56	42·0	18·87	15·33
36·7	15·57	12·61	42·1	18·93	15·38
36·8	15·63	12·66	42·2	18·99	15·43
36·9	15·70	12·71	42·3	19·05	15·48
37·0	15·76	12·77	42·4	19·11	15·53
37·1	15·82	12·83	42·5	19·17	15·58
37·2	15·89	12·87	42·6	19·23	15·63
37·3	15·95	12·92	42·7	19·29	15·69
37·4	16·01	12·97	42·8	19·36	15·74
37·5	16·08	13·03	42·9	19·42	15·79
37·6	16·14	13·08	43·0	19·48	15·84
37·7	16·20	13·13	43·1	19·54	15·89
37·8	16·26	13·18	43·2	19·60	15·94
37·9	16·33	13·23	43·3	19·66	15·99
38·0	16·39	13·28	43·4	19·72	16·04
38·1	16·45	13·33	43·5	19·79	16·09
38·2	16·51	13·38	43·6	19·85	16·14
38·3	16·57	13·44	43·7	19·91	16·19
38·4	16·64	13·49	43·8	19·97	16·24
38·5	16·70	13·54	43·9	20·03	16·29
38·6	16·76	13·59	44·0	20·09	16·34
38·7	16·83	13·64	44·1	20·15	16·39
38·8	16·89	13·69	44·2	20·21	16·44
38·9	16·95	13·74	44·3	20·27	16·49
39·0	17·01	13·79	44·4	20·33	16·55
39·1	17·07	13·85	44·5	20·39	16·60
39·2	17·14	13·90	44·6	20·45	16·65
39·3	17·20	13·95	44·7	20·52	16·70
39·4	17·26	14·00	44·8	20·58	16·75
39·5	17·32	14·05	44·9	20·64	16·80
39·6	17·39	14·10	45·0	20·70	16·85
39·7	17·45	14·15	45·1	20·76	16·90
39·8	17·51	14·21	45·2	20·82	16·95
39·9	17·57	14·26	45·3	20·88	17·00
40·0	17·63	14·31	45·4	20·94	17·05
40·1	17·70	14·36	45·5	21·00	17·10
40·2	17·76	14·41	45·6	21·06	17·15
40·3	17·82	14·46	45·7	21·12	17·20
40·4	17·88	14·51	45·8	21·18	17·25
40·5	17·94	14·56	45·9	21·24	17·30
40·6	18·01	14·62	46·0	21·30	17·35
40·7	18·07	14·67	46·1	21·36	17·40
40·8	18·13	14·72	46·2	21·42	17·45
40·9	18·19	14·77	46·3	21·48	17·50
41·0	18·25	14·82	46·4	21·54	17·55

REFRACTION OF ALCOHOL SOLUTIONS ON IMMERSION REFRACTOMETER. *PRISM 1.—Continued.*

Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.	Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.
46·5	21·60	17·60	51·9	24·90	20·36
46·6	21·66	17·65	52·0	24·96	20·41
46·7	21·72	17·70	52·1	25·03	20·46
46·8	21·78	17·75	52·2	25·09	20·52
46·9	21·84	17·80	52·3	25·15	20·57
47·0	21·90	17·85	52·4	25·21	20·62
47·1	21·96	17·90	52·5	25·28	20·67
47·2	22·02	17·95	52·6	25·34	20·72
47·3	22·08	18·01	52·7	25·40	20·78
47·4	22·15	18·06	52·8	25·46	20·83
47·5	22·21	18·11	52·9	25·53	20·88
47·6	22·27	18·16	53·0	25·59	20·93
47·7	22·33	18·21	53·1	25·65	20·98
47·8	22·39	18·26	53·2	25·71	21·04
47·9	22·45	18·31	53·3	25·77	21·09
48·0	22·51	18·36	53·4	25·84	21·14
48·1	22·57	18·41	53·5	25·90	21·20
48·2	22·63	18·46	53·6	25·96	21·25
48·3	22·69	18·51	53·7	26·03	21·30
48·4	22·75	18·56	53·8	26·09	21·36
48·5	22·81	18·61	53·9	26·15	21·41
48·6	22·87	18·66	54·0	26·22	21·47
48·7	22·93	18·71	54·1	26·28	21·52
48·8	22·99	18·76	54·2	26·34	21·57
48·9	23·06	18·81	54·3	26·41	21·63
49·0	23·12	18·86	54·4	26·47	21·68
49·1	23·18	18·91	54·5	26·53	21·73
49·2	23·24	18·96	54·6	26·59	21·79
49·3	23·30	19·02	54·7	26·66	21·84
49·4	23·36	19·07	54·8	26·72	21·90
49·5	23·42	19·12	54·9	26·78	21·95
49·6	23·48	19·17	55·0	26·85	22·00
49·7	23·55	19·22	55·1	26·91	22·05
49·8	23·61	19·27	55·2	26·97	22·11
49·9	23·67	19·32	55·3	27·04	22·16
50·0	23·73	19·38	55·4	27·10	22·21
50·1	23·79	19·43	55·5	27·16	22·26
50·2	23·85	19·48	55·6	27·23	22·32
50·3	23·91	19·53	55·7	27·29	22·37
50·4	23·98	19·58	55·8	27·35	22·42
50·5	24·04	19·63	55·9	27·41	22·48
50·6	24·10	19·69	56·0	27·48	22·53
50·7	24·16	19·74	56·1	27·54	22·58
50·8	24·22	19·79	56·2	27·60	22·64
50·9	24·28	19·84	56·3	27·66	22·69
51·0	24·35	19·89	56·4	27·73	22·74
51·1	24·41	19·94	56·5	27·79	22·79
51·2	24·47	20·00	56·6	27·85	22·85
51·3	24·53	20·05	56·7	27·91	22·90
51·4	24·59	20·10	56·8	27·98	22·95
51·5	24·65	20·15	56·9	28·04	23·01
51·6	24·72	20·20	57·0	28·10	23·06
51·7	24·78	20·26	57·1	28·16	23·11
51·8	24·84	20·31	57·2	28·23	23·17

REFRACTION OF ALCOHOL SOLUTIONS ON IMMERSION REFRACTOMETER. *PRISM 1.—Continued.*

Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.	Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.
57·3	28·29	23·22	62·7	31·76	26·17
57·4	28·35	23·27	62·8	31·83	26·23
57·5	28·42	23·33	62·9	31·89	26·29
57·6	28·48	23·38	63·0	31·96	26·35
57·7	28·54	23·43	63·1	32·03	26·41
57·8	28·60	23·49	63·2	32·10	26·46
57·9	28·67	23·54	63·3	32·17	26·52
58·0	28·73	23·59	63·4	32·23	26·58
58·1	28·79	23·65	63·5	32·30	26·64
58·2	28·86	23·70	63·6	32·37	26·70
58·3	28·92	23·75	63·7	32·44	26·76
58·4	28·98	23·81	63·8	32·51	26·82
58·5	29·04	23·86	63·9	32·58	26·88
58·6	29·11	23·91	64·0	32·65	26·94
58·7	29·17	23·97	64·1	32·72	26·99
58·8	29·23	24·02	64·2	32·79	27·05
58·9	29·30	24·08	64·3	32·86	27·11
59·0	29·36	24·13	64·4	32·92	27·17
59·1	29·42	24·18	64·5	32·99	27·23
59·2	29·49	24·24	64·6	33·06	27·29
59·3	29·55	24·29	64·7	33·13	27·35
59·4	29·61	24·34	64·8	33·20	27·41
59·5	29·68	24·40	64·9	33·27	27·47
59·6	29·74	24·45	65·0	33·34	27·53
59·7	29·80	24·50	65·1	33·41	27·59
59·8	29·87	24·56	65·2	33·48	27·65
59·9	29·93	24·61	65·3	33·55	27·71
60·0	29·99	24·67	65·4	33·62	27·77
60·1	30·06	24·72	65·5	33·69	27·83
60·2	30·12	24·77	65·6	33·76	27·89
60·3	30·19	24·83	65·7	33·83	27·95
60·4	30·25	24·88	65·8	33·90	28·01
60·5	30·32	24·94	65·9	33·97	28·07
60·6	30·38	24·99	66·0	34·04	28·13
60·7	30·45	25·04	66·1	34·11	28·19
60·8	30·51	25·10	66·2	34·18	28·26
60·9	30·57	25·16	66·3	34·25	28·32
61·0	30·64	25·21	66·4	34·33	28·38
61·1	30·70	25·27	66·5	34·40	28·45
61·2	30·77	25·32	66·6	34·47	28·51
61·3	30·83	25·38	66·7	34·54	28·57
61·4	30·90	25·44	66·8	34·62	28·64
61·5	30·96	25·49	66·9	34·69	28·70
61·6	31·03	25·55	67·0	34·76	28·76
61·7	31·09	25·60	67·1	34·83	28·82
61·8	31·16	25·66	67·2	34·91	28·89
61·9	31·23	25·71	67·3	34·98	28·95
62·0	31·29	25·77	67·4	35·05	29·01
62·1	31·36	25·83	67·5	35·13	29·08
62·2	31·43	25·88	67·6	35·20	29·14
62·3	31·49	25·94	67·7	35·28	29·21
62·4	31·56	25·99	67·8	35·35	29·27
62·5	31·63	26·05	67·9	35·43	29·34
62·6	31·69	26·11	68·0	35·50	29·41

REFRACTION OF ALCOHOL SOLUTIONS ON IMMERSION REFRACTOMETER. *PRISM 1.—Continued.*

Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.	Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.
68·1	35·57	29·47	73·5	39·93	33·30
68·2	35·65	29·54	73·6	40·02	33·37
68·3	35·72	29·60	73·7	40·10	33·45
68·4	35·80	29·67	73·8	40·19	33·53
68·5	35·87	29·73	73·9	40·28	33·60
68·6	35·95	29·80	74·0	40·36	33·68
68·7	36·02	29·86	74·1	40·45	33·76
68·8	36·10	29·93	74·2	40·53	33·83
68·9	36·18	29·99	74·3	40·62	33·91
69·0	36·25	30·06	74·4	40·71	33·98
69·1	36·33	30·13	74·5	40·79	34·06
69·2	36·41	30·20	74·6	40·88	34·14
69·3	36·48	30·27	74·7	40·97	34·22
69·4	36·56	30·33	74·8	41·05	34·30
69·5	36·64	30·40	74·9	41·14	34·38
69·6	36·72	30·47	75·0	41·23	34·46
69·7	36·79	30·54	75·1	41·32	34·54
69·8	36·87	30·61	75·2	41·41	34·61
69·9	36·95	30·67	75·3	41·50	34·69
70·0	37·02	30·74	75·4	41·58	34·77
70·1	37·10	30·81	75·5	41·67	34 85
70·2	37·19	30·88	75·6	41·76	34·93
70·3	37·27	30·95	75·7	41·85	35·01
70·4	37·35	31·01	75·8	41·94	35·09
70·5	37·43	31·09	75·9	42·03	35·17
70·6	37·51	31·16	76·0	42·12	35·25
70·7	37·59	31·23	76·1	42·21	35·33
70·8	37·67	31·30	76·2	42·30	35·41
70·9	37·75	31·37	76·3	42·39	35·50
71·0	37·83	31·44	76·4	42·48	35·58
71·1	37·91	31·51	76·5	42·57	35·66
71·2	37·99	31·59	76·6	42·66	35·74
71·3	38·07	31·66	76·7	42·75	35·82
71·4	38·16	31·73	76·8	42·84	35·90
71·5	38·24	31·80	76·9	42·93	35·98
71·6	38·32	31·87	77·0	43·02	36·07
71·7	38·40	31·94	77·1	43·11	36·15
71·8	38·49	32·01	77·2	43·20	36·24
71·9	38·57	32·09	77·3	43·30	36·32
72·0	38·65	32·17	77·4	43·39	36·40
72·1	38·74	32·24	77·5	43·48	36·49
72·2	38·82	32·32	77·6	43·57	36·57
72·3	38·90	32·39	77·7	43·67	36·66
72·4	38·98	32·47	77·8	43·76	36 74
72·5	39·07	32·54	77·9	43·85	36·82
72·6	39·16	32·62	78·0	43·94	36·91
72·7	39·24	32·69	78·1	44·04	36·99
72·8	39·33	32·77	78 2	44·13	37·08
72 9	39·41	32·84	78·3	44·23	37·16
73 0	39·50	32·92	78·4	44·32	37·25
73·1	39·59	32·99	78·5	44·42	37·33
73·2	39·67	33·07	78·6	44·51	37·42
73·3	39·76	33·15	78·7	44·60	37·50
73·4	39 84	33 22	78·8	44·70	37·59

REFRACTION OF ALCOHOL SOLUTIONS ON IMMERSION REFRACTOMETER. *PRISM 1.—Continued.*

Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.	Scale Reading.	Per cent. by Volume, at 20° C.	Per cent. by Weight, at 20° C.
78·9	44·79	37·68	79·5	45·38	38·20
79·0	44·89	37·76	79·6	45·48	38·30
79·1	44·98	37·85	79·7	45·58	38·39
79·2	45·08	37·94	79·8	45·68	38·48
79·3	45·18	38·02	79·9	45·78	38·57
79·4	45·28	38·11	80·0	45·88	38·67

REFRACTION OF METHYL AND ETHYL ALCOHOLS ON THE IMMERSION REFRACTOMETER. *PRISM 1.*

Per cent. Alcohol by Weight.	Scale Readings.		Per cent. Alcohol by Weight.	Scale Readings.		Per cent. Alcohol by Weight.	Scale Readings.	
	Methyl Alcohol.	Ethyl Alcohol.		Methyl Alcohol.	Ethyl Alcohol.		Methyl Alcohol.	Ethyl Alcohol.
0	14·5	14·5	34	35·2	74·4	68	34·0	99·4
1	14·8	16·0	35	35·8	75·8	69	33·5	99·7
2	15·4	17·6	36	36·3	76·9	70	33·0	100·0
3	16·0	19·1	37	36·8	78·0	71	32·3	100·2
4	16·6	20·7	38	37·3	79·1	72	31·7	100·4
5	17·2	22·3	39	37·7	80·2	73	31·0	100·6
6	17·8	24·1	40	38·1	81·3	74	30·4	100·8
7	18·4	25·9	41	38·4	82·3	75	29·7	101·0
8	19·0	27·8	42	38·8	83·3	76	29·0	101·0
9	19·6	29·6	43	39·2	84·2	77	28·3	100·9
10	20·2	31·4	44	39·3	85·2	78	27·6	100·9
11	20·8	33·2	45	39·4	86·2	79	26·8	100·8
12	21·4	35·0	46	39·5	87·0	80	26·0	100·7
13	22·0	36·9	47	39·6	87·8	81	25·1	100·6
14	22·6	38·7	48	39·7	88·7	82	24·3	100·5
15	23·2	40·5	49	39·8	89·5	83	23·6	100·4
16	23·9	42·5	50	39·8	90·3	84	22·8	100·3
17	24·5	44·5	51	39·7	91·1	85	21·8	100·1
18	25·2	46·5	52	39·6	91·8	86	20·8	99·8
19	25·8	48·5	53	39·6	92·4	87	19·7	99·5
20	26·5	50·5	54	39·5	93·0	88	18·6	99·2
21	27·1	52·4	55	39·4	93·6	89	17·3	98·9
22	27·8	54·3	56	39·2	94·1	90	16·1	98·6
23	28·4	56·3	57	39·0	94·7	91	14·9	98·3
24	29·1	58·2	58	38·6	95·2	92	13·7	97·8
25	29·7	60·1	59	38·3	95·7	93	12 4	97·2
26	30·3	61·9	60	37·9	96·2	94	11·0	96·4
27	30·9	63·7	61	37·5	96·7	95	9·6	95·7
28	31·6	65·5	62	37·0	97·1	96	8·2	94·9
29	32·2	67·2	63	36·5	97·5	97	6·7	94·0
30	32·8	69·0	64	36·0	98·0	98	3·5	93·0
31	33·5	70·4	65	35·5	98·3	99	3·5	92·0
32	34·1	71·7	66	35·0	98·7	100	2 0	91·0
33	34·7	73·1	67	34·5	99·1			

REFRACTIVE INDICES. (*Sodium D Line at* 15° *C.*)

	n—1.		n—1.
Acetic acid	0·374	Ethyl alcohol	0·363
„ anhydride	0·392	„ ether	0·355
Acetone	0·361	Ethylene dibromide	0·541
Amyl acetate	0·406	Glycerin	0·475
„ alcohol (*iso*)	0·409	Methyl alcohol	0·331
Aniline	0·589	Methylene iodide	0·744
Benzene	0·504	Naphthalene bromide	0·660
Benzyl alcohol	0·541	Nitrobenzene	0·554
Bromoform	0·591	Phenol	0·552
Canada balsam	0·530	Pyridine	0·509
Carbon disulphide	0·631	Sulphuric acid	0·420
„ tetrachloride	0·463	Toluene	0·498
Chloroform	0·449	Water	0·333
Ethyl acetate	0·374	Xylene	0·499

CONVERSION OF SCALE READINGS OF DIPPING REFRACTOMETER INTO REFRACTIVE INDICES. *PRISM 1.*

Scale Reading.	n_D=1·3.	Scale Reading.	n_D=1·3.	Scale Reading.	n_D=1·3.
−5	2539	32	3972	69	5352
−4	2578	33	4010	70	5388
−3	2618	34	4048	71	5425
−2	2657	35	4086	72	5461
−1	2696	36	4124	73	5497
0	2736	37	4162	74	5533
1	2775	38	4199	75	5569
2	2814	39	4237	76	5606
3	2854	40	4275	77	5642
4	2893	41	4313	78	5678
5	2932	42	4350	79	5714
6	2971	43	4388	80	5750
7	3010	44	4426	81	5786
8	3049	45	4463	82	5822
9	3087	46	4500	83	5858
10	3126	47	4537	84	5894
11	3165	48	4575	85	5930
12	3204	49	4612	86	5966
13	3242	50	4650	87	6002
14	3281	51	4687	88	6038
15	3320	52	4724	89	6074
16	3358	53	4761	90	6109
17	3397	54	4798	91	6145
18	3435	55	4836	92	6181
19	3474	56	4873	93	6217
20	3513	57	4910	94	6252
21	3551	58	4947	95	6287
22	3590	59	4984	96	6323
23	3628	60	5021	97	6359
24	3667	61	5058	98	6394
25	3705	62	5095	99	6429
26	3743	63	5132	100	6464
27	3781	64	5169	101	6500
28	3820	65	5205	102	6535
29	3858	66	5242	103	6570
30	3896	67	5279	104	6605
31	3934	68	5316	105	6640

EXAMPLE: Scale division 3 corresponds to Refractive Index (n_D)=1·32854.

EQUIVALENTS OF INDICES OF REFRACTION AND BUTYRO REFRACTOMETER READINGS.

Refractive Index (n_D).	Scale Readings. Fourth Decimal of n_D.									
	0	1	2	3	4	5	6	7	8	9
1·422	0·0	0·1	0·2	0·4	0·5	0·6	0·7	0·9	1·0	1·1
1·423	1·2	1·4	1·5	1·6	1·7	1·9	2·0	2·1	2·2	2·4
1·424	2·5	2·6	2·7	2·8	3·0	3·1	3·2	3·3	3·5	3·6
1·425	3·7	3·8	4·0	4·1	4·2	4·3	4·5	4·6	4·7	4·8
1·426	5·0	5·1	5·2	5·4	5·5	5·6	5·7	5·9	6·0	6·1
1·427	6·2	6·4	6·5	6·6	6·8	6·9	7·0	7·1	7·2	7·4
1·428	7·5	7·6	7·7	7·9	8·0	8·1	8·2	8·4	8·5	8·6
1·429	8·7	8·9	9·0	9·1	9·2	9·4	9·5	9·6	9·8	9·9
1·430	10·0	10·1	10·3	10·4	10·5	10·6	10·7	10·9	11·0	11·1
1·431	11·3	11·4	11·5	11·6	11·8	11·9	12·0	12·2	12·3	12·4
1·432	12·5	12·7	12·8	12·9	13·0	13·2	13·3	13·5	13·6	13·7
1·433	13·8	14·0	14·1	14·2	14·4	14·5	14·6	14·7	14·9	15·0
1·434	15·1	15·3	15·4	15·5	15·6	15·8	15·9	16·0	16·2	16·3
1·435	16·4	16·6	16·7	16·8	17·0	17·1	17·2	17·4	17·5	17·6
1·436	17·8	17·9	18·0	18·2	18·3	18·4	18·5	18·7	18·8	19·0
1·437	19·1	19·2	19·3	19·5	19·6	19·7	19·8	20·0	20·1	20·2
1·438	20·4	20·5	20·6	20·8	20·9	21·1	21·2	21·3	21·4	21·6
1·439	21·7	21·8	22·0	22·1	22·2	22·4	22·5	22·6	22·7	22·9
1·440	23·0	23·2	23·3	23·4	23·5	23·7	23·8	23·9	24·1	24·2
1·441	24·3	24·5	24·6	24·7	24·8	25·0	25·1	25·2	25·4	25·5
1·442	25·6	25·8	25·9	26·1	26·2	26·3	26·5	26·6	26·7	26·9
1·443	27·0	27·1	27·3	27·4	27·5	27·7	27·8	27·9	28·1	28·2
1·444	28·3	28·5	28·6	28·7	28·9	29·0	29·2	29·3	29·4	29·6
1·445	29·7	29·9	30·0	30·1	30·3	30·4	30·6	30·7	30·8	30·9
1·446	31·1	31·2	31·4	31·5	31·6	31·8	31·9	32·1	32·2	32·3
1·447	32·5	32·6	32·8	32·9	33·0	33·2	33·3	33·5	33·6	33·7
1·448	33·9	34·0	34·2	34·3	34·4	34·6	34·7	34·9	35·0	35·1
1·449	35·3	35·4	35·6	35·7	35·8	36·0	36·1	36·3	36·4	36·5
1·450	36·7	36·8	37·0	37·1	37·2	37·4	37·5	37·7	37·8	37·9
1·451	38·1	38·2	38·3	38·5	38·6	38·7	38·9	39·0	39·2	39·3
1·452	39·5	39·6	39·7	39·9	40·0	40·1	40·3	40·4	40·6	40·7
1·453	40·9	41·0	41·1	41·3	41·4	41·5	41·7	41·8	42·0	42·1
1·454	42·3	42·4	42·5	42·7	42·8	43·0	43·1	43·3	43·4	43·6
1·455	43·7	43·9	44·0	44·2	44·3	44·4	44·6	44·7	44·9	45·0
1·456	45·2	45·3	45·5	45·6	45·7	45·9	46·0	46·2	46·3	46·4
1·457	46·6	46·7	46·9	47·0	47·2	47·3	47·5	47·6	47·7	47·9
1·458	48·0	48·2	48·3	48·5	48·6	48·8	48·9	49·1	49·2	49·4
1·459	49·5	49·7	49·8	50·0	50·1	50·2	50·4	50·5	50·7	50·8
1·460	51·0	51·1	51·3	51·4	51·6	51·7	51·9	52·0	52·2	52·3
1·461	52·5	52·7	52·8	53·0	53·1	53·3	53·4	53·6	53·7	53·9
1·462	54·0	54·2	54·3	54·5	54·6	54·8	55·0	55·1	55·3	55·4
1·463	55·6	55·7	55·9	56·0	56·2	56·3	56·5	56·6	56·8	56·9
1·464	57·1	57·3	57·4	57·6	57·7	57·9	58·0	58·2	58·3	58·5
1·465	58·6	58·8	58·9	59·1	59·2	59·4	59·5	59·7	59·8	60·0
1·466	60·2	60·3	60·5	60·6	60·8	60·9	61·1	61·2	61·4	61·5
1·467	61·7	61·8	62·0	62·2	62·3	62·5	62·6	62·8	62·9	63·1
1·468	63·2	63·4	63·5	63·7	63·8	64·0	64·2	64·3	64·5	64·7
1·469	64·8	65·0	65·1	65·3	65·4	65·6	65·7	65·9	66·2	66·3
1·470	66·4	66·5	66·7	66·8	67·0	67·2	67·3	67·5	67·7	67·8
1·471	68·0	68·1	68·3	68·4	68·6	68·7	68·9	69·1	69·2	69·4
1·472	69·5	69·7	69·9	70·0	70·2	70·3	70·5	70·7	70·8	71·0

EQUIVALENTS OF INDICES OF REFRACTION AND BUTYRO REFRACTOMETER READINGS.—*Continued.*

Refractive Index (n_D).	Scale Readings. Fourth Decimal of n_D.									
	0	1	2	3	4	5	6	7	8	9
1·473	71·1	71·3	71·4	71·6	71·8	71·9	72·1	72·2	72·4	72·5
1·474	72·7	72·9	73·0	73·2	73·3	73·5	73·7	73·8	74·0	74·1
1·475	74·3	74·5	74·6	74·8	75·0	75·1	75·3	75·5	75·6	75·8
1·476	76·0	76·1	76·3	76·5	76·7	76·8	77·0	77·2	77·3	77·5
1·477	77·7	77·9	78·1	78·2	78·4	78·6	78·7	78·9	79·1	79·2
1·478	79·4	79·6	79·8	80·0	80·1	80·3	80·5	80·6	80·8	81·0
1·479	81·2	81·3	81·5	81·7	81·9	82·0	82·2	82·4	82·5	82·7
1·480	82·9	83·1	83·2	83·4	83·6	83·8	83·9	84·1	84·3	84·5
1·481	84·6	84·8	85·0	85·1	85·2	85·3	85·5	85·7	86·0	86·2
1·482	86·4	86·6	86·7	86·9	87·1	87·3	87·5	87·6	87·8	88·0
1·483	88·2	88·3	88·5	88·7	88·9	89·1	89·2	89·4	89·6	89·8
1·484	90·0	90·2	90·3	90·5	90·7	90·9	91·1	91·2	91·4	91·6
1·485	91·8	92·0	92·1	92·3	92·5	92·7	92·9	93·0	93·2	93·4
1·486	93·6	93·8	94·0	94·1	94·3	94·5	94·7	94·8	95·0	95·2
1·487	95·4	95·6	95·8	96·0	96·1	96·3	96·5	96·7	96·9	97·0
1·488	97·2	97·4	97·6	97·8	98·0	98·1	98·3	98·5	98·7	98·9
1·489	99·1	99·2	99·4	99·6	99·8	100·0	..	..	..	..

TABLES FOR SUGAR ANALYSIS BY LANE AND EYNON'S METHOD

(*Using* 25 *cc. Mixed Fehling Solution.*)

Milligrams per 100 cc.

Cc. Sugar Solution required.	Invert Sugar.	Invert Sugar and Sucrose.	Anhydrous Dextrose.	Anhydrous Lævulose.	Maltose.		Lactose.	
					Hydrated.	Anhydrous.	Hydrated.	Anhydrous.
15·0	824·0	817·0	801·0	849·0	1388·0	1319·0	1150·0	1093·0
15·5	798·0	792·0	776·0	822·5	1343·0	1276·0	1113·0	1057·5
16·0	772·0	767·0	751·0	796·0	1298·0	1233·0	1076·0	1022·0
16·5	749·5	744·0	729·0	773·0	1259·0	1196·0	1043·0	991·0
17·0	727·0	721·0	707·0	750·0	1220·0	1159·0	1010·0	960·0
17·5	707·0	701·5	687·5	729·0	1185·5	1126·0	981·0	933·0
18·0	687·0	682·0	668·0	708·0	1151·0	1093·0	952·0	906·0
18·5	669·0	664·0	650·5	690·0	1119·5	1063·5	926·0	880·5
19·0	651·0	646·0	633·0	672·0	1088·0	1034·0	900·0	855·0
19·5	635·0	630·0	617·2	655·0	1060·1	1007·3	877·2	833·4
20·0	619·0	614·0	601·5	638·0	1032·3	980·7	854·5	811·8
20·5	604·2	599·4	587·2	623·0	1006·9	956·6	833·4	792·0

TABLES FOR SUGAR ANALYSIS BY LANE AND EYNON'S METHOD.—*Continued.*

(*Using* 25 *cc. Mixed Fehling Solution.*)

Milligrams per 100 cc.

Cc. Sugar Solution required.	Invert Sugar.	Invert Sugar and Sucrose.	Anhydrous Dextrose.	Anhydrous Lævulose.	Maltose.		Lactose.	
					Hydrated.	Anhydrous.	Hydrated.	Anhydrous.
21·0	589·5	584·6	572·9	608·1	981·6	932·5	812·4	772·5
21·5	576·3	571·5	560·1	594·3	958·5	910·6	793·4	754·0
22·0	563·2	558·2	547·3	580·6	935·5	888·7	774·5	735·8
22·5	550·9	546·1	535·4	568·0	914·3	868·6	757·2	719·4
23·0	538·7	534·0	523·6	555·5	893·2	848·5	740·0	703·0
23·5	527·7	523·0	512·7	544·0	873·8	830·1	724·2	688·0
24·0	516·7	512·1	501·9	532·5	854·5	811·8	708·5	673·1
24·5	506·3	502·0	491·9	522·0	836·7	794·9	694·0	659·3
25·0	496·0	492·0	482·0	511·5	819·0	778·1	679·5	645·5
25·5	486·6	482·5	472·8	501·7	802·6	762·5	666·1	632·8
26·0	477·3	473·1	463·7	491·9	786·3	747·0	652·7	620·1
26·5	468·5	464·3	455·2	482·9	771·1	732·6	640·3	608·3
27·0	459·7	455·6	446·8	474·0	756·0	718·2	627·9	596·5
27·5	451·6	447·6	438·9	465·6	741·9	704·8	616·3	585·5
28·0	443·6	439·6	431·1	457·2	727·9	691·5	604·8	574·6
28·5	435·9	432·0	423·7	449·4	714·8	679·0	594·0	564·3
29·0	428·3	424·4	416·4	441·6	701·7	666·6	583·3	554·1
29·5	421·3	417·4	409·5	434·3	689·5	655·0	573·3	544·6
30·0	414·3	410·4	402·7	427·0	677·3	643·4	563·3	535·1
30·5	407·6	403·9	396·2	420·1	665·8	632·5	554·0	526·3
31·0	401·0	397·4	389·7	413·3	654·3	621·6	544·8	517·6
31·5	394·8	391·2	383·6	406·9	643·7	611·5	536·1	509·3
32·0	388·7	385·0	377·6	400·5	633·1	601·4	527·4	501·0
32·5	382·8	379·2	371·9	394·5	623·0	591·9	519·2	493·2
33·0	377·0	373·4	366·3	388·5	613·0	582·4	511·0	485·5
33·5	371·6	368·0	360·9	382·9	603·6	573·5	503·3	478·1
34·0	366·2	362·6	355·6	377·3	594·3	564·6	495·6	470·8
34·5	361·0	357·4	350·6	372·0	585·4	556·1	488·3	463·9
35·0	355·8	352·3	345·6	366·7	576·5	547·7	481·1	457·0
35·5	350·9	347·4	340·9	361·7	568·1	539·7	474·2	450·4
36·0	346·1	342·5	336·3	356·6	559·7	531·7	467·3	443·9
36·5	341·4	338·0	331·8	351·8	551·8	524·2	460·8	437·7
37·0	336·8	333·5	327·4	347·0	543·9	516·7	454·3	431·6
37·5	332·4	329·1	323·1	342·5	536·4	509·6	448·2	425·8
38·0	328·1	324·7	318·8	338·1	528·9	502·5	442·1	420·0
38·5	323·9	320·5	314·7	333·8	521·8	495·7	436·3	414·5
39·0	319·7	316·4	310·7	329·6	514·7	489·0	430·5	409·0
39·5	315·8	312·5	306·9	325·5	508·0	482·6	425·0	403·7
40·0	311·9	308·6	303·1	321·5	501·3	476·2	419·5	398·5
40·5	308·1	304·9	299·5	317·6	494·9	470·1	414·2	393·5
41·0	304·4	301·2	295·9	313·7	488·5	464·1	409·0	388·6
41·5	300·8	297·6	292·4	309·9	482·4	458·3	404·0	383·8
42·0	297·3	294·1	289·0	306·2	476·3	452·5	399·1	379·1
42·5	293·9	290·7	285·7	302·7	470·5	447·0	394·4	374·6
43·0	290·5	287·3	282·4	299·2	464·7	441·5	389·7	370·2

TABLES FOR SUGAR ANALYSIS BY LANE AND EYNON'S METHOD.—*Continued.*

(*Using* 25 *cc. Mixed Fehling Solution.*)

Milligrams per 100 cc.

Cc. Sugar Solution re-quired.	Invert Sugar.	Invert Sugar and Sucrose.	An-hydrous Dextrose.	An-hydrous Lævulose.	Maltose.		Lactose.	
					Hy-drated.	An-hydrous.	Hy-drated.	An-hydrous.
43·5	287·3	284·1	279·2	295·8	459·1	436·2	385·2	365·9
44·0	284·1	280·9	276·1	292·5	453·6	430·9	380·7	361·7
44·5	281·0	277·8	273·1	289·3	448·3	425·9	376·4	357·6
45·0	277·9	274·7	270·1	286·2	443·0	420·9	372·1	353·5
45·5	274·9	271·7	267·2	283·1	438·0	416·1	368·0	349·6
46·0	272·0	268·7	264·3	280·0	433·1	411·4	363·9	345·7
46·5	269·1	265·9	261·5	277·1	428·3	406·9	359·9	341·9
47·0	266·3	263·1	258·8	274·2	423·6	402·4	356·0	338·2
47·5	263·5	260·4	256·1	271·4	419·0	398·0	352·1	334·5
48·0	260·8	257·7	253·5	268·6	414·4	393·7	348·3	330·9
48·5	258·1	255·1	250·9	265·9	409·9	389·4	344·6	327·4
49·0	255·5	252·5	248·4	263·2	405·5	385·2	341·0	324·0
49·5	253·0	250·0	246·0	260·6	401·3	381·2	337·6	320·7
50·0	250·6	247·6	243·6	258·0	397·2	377·3	334·2	317·5

SOLUTION FACTORS OF SUGARS AT VARIO

S.G. at 15·5° C.	Dextrose.	Sucrose.	Invert Sugar.	Lævulose.	
1010	3·845	3·869	3·895	3·940	3·938
1020	3·841	3·867	3·892	3·932	3·934
1030	3·837	3·865	3·890	3·925	3·929
1040	3·832	3·863	3·887	3·918	3·924
1050	3·827	3·860	3·884	3·910	3·919
1060	3·821	3·857	3·881	3·903	3·913
1070	3·814	3·854	3·878	3·895	3·907
1080	3·807	3·850	3·875	3·887	3·902
1090	3·799	3·847	3·872	3·880	3·895
1100	3·791	3·842	3·869	3·871	3·889
1110	..	..	3·865	..	3·883
1120	..	..	3·862	..	3·876
1130	..	..	3·858	..	3·869
1140	..	..	3·854	..	3·862

QUANTITIES OF COPPER AND COPPER OXIDE PRODUCED UNDER STANDARD CONDITIONS BY VARIOUS CARBOHYDRATES.[1]

(*Quantities expressed in Milligrams in all cases.*)

Cupric Oxide.	Cuprous Oxide.	Copper.	Dextrose.	Starch.	Lævulose.	Hydrated Lactose, $C_{12}H_{22}O_{11}, H_2O$.	Anhydrous Lactose.	Maltose.	Invert Sugar.	Cane Sugar.
100	89·9	79·9	..	..	..	59·2	56·2	72·5	..	..
110	98·9	87·9	..	..	..	65·2	61·9	79·8	45·3	43·0
120	107·9	95·9	46·5	41·8	51·7	71·2	67·6	87·2	49·2	46·7
130	116·9	103·9	50·4	45·4	55·5	77·2	73·3	95·3	53·1	50·4
140	125·9	111·9	54·2	48·8	59·5	83·2	79·0	102·0	57·0	54·2
150	134·9	119·8	58·0	52·2	63·9	89·3	84·8	109·2	61·0	58·0
160	143·9	127·8	61·8	55·6	68·1	95·4	90·6	116·8	65·1	61·8
170	152·9	135·8	65·7	59·1	72·4	101·4	96·3	124·2	69·2	65·7
180	161·9	143·8	69·6	62·6	76·7	107·4	102·0	131·5	73·4	69·7
190	170·9	151·8	73·6	66·2	80·9	113·5	107·9	138·8	77·5	73·6
200	179·9	159·8	77·6	69·8	85·3	119·7	113·7	146·3	81·5	77·4
210	188·9	167·8	81·6	73·4	89·5	126·0	119·7	153·6	85·7	81·4
220	197·9	175·8	85·5	77·0	94·0	132·2	125·6	161·0	90·0	85·5
230	206·9	183·8	90·0	81·0	98·6	138·4	131·5	168·3	94·4	89·7
240	215·9	191·7	94·2	84·8	103·0	144·6	137·4	175·7	98·7	93·8
250	224·9	199·7	98·3	88·5	107·3	150·7	143·2	183·1	102·9	97·8
260	233·9	207·7	102·5	92·3	111·8	157·0	149·2	190·5	107·1	101·7
270	242·9	215·7	106·7	96·0	116·4	163·0	154·9	197·9	111·4	105·8
280	251·9	223·7	110·8	99·7	121·0	169·2	160·7	205·2	115·7	109·9
290	260·8	231·7	115·0	103·5	125·6	175·5	166·7	212·6	120·1	114·1
300	269·8	239·7	119·4	107·5	130·1	182·3	173·2	220·0	124·6	118·4
310	278·8	247·7	123·7	111·3	134·7	188·9	179·5	227·3	129·1	122·6
320	287·8	255·7	128·2	115·4	139·5	195·4	185·6	234·7	133·7	127·0
330	296·8	263·6	132·6	119·3	144·5	202·0	191·9	242·1	138·2	131·3
340	305·8	271·6	137·1	123·4	149·5	208·7	198·3	249·5	142·8	135·7
350	314·8	279·6	141·7	127·5	154·2	215·3	204·5	256·9	147·7	140·3
360	323·8	287·6	146·4	131·8	158·9	222·0	210·9	264·3	152·7	145·1
370	332·8	295·6	151·2	136·1	163·8	228·6	217·2	271·6	157·5	149·6
380	341·8	303·6	155·6	140·1	168·5	235·2	223·4	279·0	161·9	153·8
390	350·8	311·6	160·5	144·5	173·5	241·9	229·8	286·4	166·5	158·2
400	359·8	319·6	165·2	148·7	178·4	248·6	236·2	293·7	171·4	162·8
410	368·8	327·6	170·1	153·1	183·3	254·7	242·0	301·1	176·2	167·2
420	377·8	335·5	175·0	157·5	188·3	260·9	247·9	..	181·2	172·1
430	386·8	343·5	179·9	161·9	193·2	267·2	253·8	..	186·2	176·9
440	395·8	351·5	185·0	166·5	198·4	273·8	260·1	..	191·2	181·7
450	404·8	359·5	190·0	171·0	203·6	280·4	266·4	..	196·3	186·5
460	413·8	367·5	195·0	175·5	208·8	287·2	272·8	..	201·6	191·5

[1] Elsdon, *Analyst*, 1923, 48, 435.

DENSITY OF STRONG ACIDS AT 15° C. IN VACUO.

Specific Gravity at $\frac{15° C.}{4° C.}$ (*Vacuo*).	Per cent. by Weight.			Specific Gravity at $\frac{15° C.}{4° C.}$ (*Vacuo*).	Per cent. by Weight.	
	HCl.	HNO_3.	H_2SO_4.		HNO_3.	H_2SO_4.
1·000	0·16	0·10	0·09	1·235	37·51	31·70
1·005	1·15	1·00	0·95	1·240	38·27	32·28
1·010	2·14	1·90	1·57	1·245	39·03	32·86
1·015	3·12	2·80	2·30	1·250	39·80	33·43
1·020	4·13	3·70	3·03	1·255	40·56	34·00
1·025	5·15	4·60	3·76	1·260	41·32	34·57
1·030	6·15	5·50	4·49	1·265	42·08	35·14
1·035	7·15	6·38	5·23	1·270	42·85	35·71
1·040	8·16	7·26	5·96	1·275	43·62	36·29
1·045	9·16	8·13	6·67	1·280	44·39	36·87
1·050	10·17	8·99	7·37	1·285	45·16	37·45
1·055	11·18	9·84	8·07	1·290	45·93	38·03
1·060	12·19	10·67	8·77	1·295	46·70	38·61
1·065	13·19	11·50	9·47	1·300	47·47	39·19
1·070	14·17	12·32	10·19	1·305	48·24	39·77
1·075	15·16	13·14	10·90	1·310	49·05	40·35
1·080	16·15	13·94	11·60	1·315	49·88	40·93
1·085	17·13	14·73	12·30	1·320	50·69	41·50
1·090	18·11	15·52	12·99	1·325	51·51	42·08
1·095	19·06	16·31	13·67	1·330	52·34	42·66
1·100	20·01	17·10	14·35	1·335	53·17	43·20
1·105	20·97	17·88	15·03	1·340	54·04	43·74
1·110	21·92	18·66	15·71	1·345	54·90	44·28
1·115	22·86	19·44	16·36	1·350	55·76	44·82
1·120	23·82	20·22	17·01	1·355	56·63	45·35
1·125	24·78	20·99	17·66	1·360	57·54	45·88
1·130	25·75	21·76	18·31	1·365	58·45	46·41
1·135	26·70	22·53	18·96	1·370	59·36	46·94
1·140	27·66	23·30	19·61	1·375	60·27	47·47
1·145	28·61	24·07	20·26	1·380	61·24	48·00
1·150	29·57	24·83	20·91	1·385	62·21	48·53
1·155	30·55	25·59	21·55	1·390	63·20	49·06
1·160	31·52	26·35	22·19	1·395	64·22	49·59
1·165	32·49	27·11	22·83	1·400	65·27	50·11
1·170	33·46	27·87	23·47	1·405	66·37	50·63
1·175	34·42	28·62	24·12	1·410	67·47	51·15
1·180	35·39	29·37	24·76	1·415	68·60	51·66
1·185	36·31	30·12	25·40	1·420	69·77	52·15
1·190	37·23	30·87	26·04	1·425	70·95	52·63
1·195	38·16	31·60	26·68	1·430	72·14	53·11
1·200	39·11	32·34	27·32	1·435	73·35	53·59
1·205	..	33·07	27·95	1·440	74·64	54·07
1·210	..	33·80	28·58	1·445	75·94	54·55
1·215	..	34·53	29·21	1·450	77·24	55·03
1·220	..	35·26	29·84	1·455	78·56	55·50
1·225	..	36·01	30·48	1·460	79·94	55·97
1·230	..	36·76	31·11	1·465	81·38	56·43

DENSITY OF STRONG ACIDS AT 15° C. IN VACUO.—*Continued.*

Specific Gravity at $\frac{15° C.}{4° C.}$ (*Vacuo*).	Per cent. by Weight. HNO_3.	Per cent. by Weight. H_2SO_4.	Specific Gravity at $\frac{15° C.}{4° C.}$ (*Vacuo*).	Per cent. by Weight, H_2SO_4.	Specific Gravity at $\frac{15° C.}{4° C.}$ (*Vacuo*).	Per cent. by Weight, H_2SO_4.
1·470	82·86	56·90	1·610	69·56	1·750	81·56
1·475	84·41	57·37	1·615	70·00	1·755	82·00
1·480	86·01	57·83	1·620	70·42	1·760	82·44
1·485	87·66	58·28	1·625	70·85	1·765	83·01
1·490	89·86	58·74	1·630	71·27	1·770	83·51
1·495	91·56	59·22	1·635	71·70	1·775	84·02
1·500	94·04	59·70	1·640	72·12	1·780	84·50
1·505	96·34	60·18	1·645	72·55	1·785	85·10
1·510	98·05	60·65	1·650	72·96	1·790	85·70
1·515	99·02	61·12	1·655	73·40	1·795	86·30
1·520	99·62	61·59	1·660	73·81	1·800	86·92
1·525	..	62·06	1·665	74·24	1·805	87·60
1·530	..	62·53	1·670	74·66	1·810	88·30
1·535	..	63·00	1·675	75·08	1·815	89·16
1·540	..	63·43	1·680	75·50	1·820	90·05
1·545	..	63·85	1·685	75·94	1·825	91·00
1·550	..	64·26	1·690	76·38	1·830	92·10
1·555	..	64·67	1·695	76·76	1·835	93·56
1·560	..	65·20	1·700	77·17	1·840	95·60
1·565	..	65·65	1·705	77·60	1·8405	95·95
1·570	..	66·09	1·710	78·04	1·8410	96·38
1·575	..	66·53	1·715	78·48	1·8415	97·35
1·580	..	66·95	1·720	78·92	1·8410	98·20
1·585	..	67·40	1·725	79·36	1·8405	98·52
1·590	..	67·83	1·730	79·80	1·8400	98·72
1·595	..	68·26	1·735	80·24	1·8395	98·77
1·600	..	68·70	1·740	80·68	1·8390	99·12
1·605	..	69·13	1·745	81·12	1·8385	99·31

DENSITY OF AQUEOUS SOLUTIONS OF ACETIC ACID.

(*Gm. per cent.=gm. of Acid in* 100 *gm. of Solution.*)

Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$
1	1·0007	11	157	21	298	31	424
2	022	12	171	22	311	32	436
3	037	13	185	23	324	33	447
4	052	14	200	24	337	34	459
5	067	15	214	25	350	35	470
6	083	16	228	26	1·0363	36	481
7	098	17	242	27	375	37	492
8	113	18	256	28	388	38	502
9	127	19	270	29	400	39	513
10	142	20	284	30	412	40	523

DENSITY OF AQUEOUS SOLUTIONS OF ACETIC ACID.—*Continued.*

(*Gm. per cent.=gm. of Acid in* 100 *gm. of Solution.*)

Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{4° C.}$
41	533	56	660	71	737	86	736
42	543	57	666	72	740	87	731
43	552	58	673	73	742	88	726
44	562	59	679	74	744	89	720
45	571	60	685	75	746	90	713
46	580	61	691	76	1·0747	91	705
47	589	62	697	77	748	92	696
48	598	63	702	78	748	93	686
49	607	64	707	79	748	94	674
50	615	65	712	80	748	95	660
51	1·0623	66	717	81	747	96	644
52	631	67	721	82	746	97	625
53	638	68	725	83	744	98	604
54	646	69	729	84	742	99	580
55	653	70	733	85	739	100	553

DENSITY OF AMMONIA SOLUTIONS AT 15° C.

Specific Gravity.	Per cent. NH_3.	Specific Gravity.	Per cent. NH_3.
1·000	0·00	0·940	15·63
0·998	0·45	0·938	16·22
0·996	0·91	0·936	16·82
0·994	1·37	0·934	17·42
0·992	1·84	0·932	18·03
0·990	2·31	0·930	18·64
0·988	2·80	0·928	19·25
0·986	3·30	0·926	19·87
0·984	3·80	0·924	20·49
0·982	4·30	0·922	21·12
0·980	4·80	0·920	21·75
0·978	5·30	0·918	22·39
0·976	5·80	0·916	23·03
0·974	6·30	0·914	23·68
0·972	6·80	0·912	24·33
0·970	7·31	0·910	24·99
0·968	7·82	0·908	25·65
0·966	8·33	0·906	26·31
0·964	8·84	0·904	26·98
0·962	9·35	0·902	27·65
0·960	9·91	0·900	28·33
0·958	10·47	0·898	29·01
0·956	11·03	0·896	29·69
0·954	11·60	0·894	30·37
0·952	12·17	0·892	31·05
0·950	12·74	0·890	31·75
0·948	13·31	0·888	32·50
0·946	13·88	0·886	33·25
0·944	14·46	0·884	34·10
0·942	15·04	0·882	34·95

DENSITY OF POTASSIUM AND SODIUM HYDROXIDE SOLUTIONS AT 15° C.

Specific Gravity.	Per cent. KOH.	Per cent. NaOH.	Specific Gravity.	Per cent. KOH.	Per cent. NaOH.
1·007	0·9	0·59	1·252	27·0	22·50
1·014	1·7	1·20	1·263	28·2	23·50
1·022	2·6	1·65	1·274	28·9	24·48
1·029	3·5	2·50	1·285	29·8	25·50
1·037	4·5	3·22	1·297	30·7	26·58
1·045	5·6	3·79	1·308	31·8	27·65
1·052	6·4	4·50	1·320	32·7	28·83
1·060	7·4	5·20	1·332	33·7	30·00
1·067	8·2	5·86	1·345	34·9	31·20
1·075	9·2	6·58	1·357	35·9	32·50
1·083	10·1	7·30	1·370	36·9	33·73
1·091	10·9	8·07	1·383	37·8	35·00
1·100	12·0	8·78	1·397	38·9	36·36
1·108	12·9	9·50	1·410	39·9	37·65
1·116	13·8	10·30	1·424	40·9	39·06
1·125	14·8	11·06	1·438	42·1	40·47
1·134	15·7	11·90	1·453	43·4	42·02
1·142	16·5	12·69	1·468	44·6	43·58
1·152	17·6	13·50	1·483	45·8	45·16
1·162	18·6	14·35	1·498	47·1	47·73
1·171	19·5	15·15	1·514	48·3	48·41
1·180	20·5	16·00	1·530	49·4	50·10
1·190	21·4	16·91	1·546	50·6	..
1·200	22·4	17·81	1·563	51·9	..
1·210	23·3	18·71	1·580	53·2	..
1·220	24·2	19·65	1·597	54·5	..
1·231	25·1	20·69	1·615	55·9	..
1·241	26·1	21·55	1·634	57·5	..

SPECIFIC GRAVITY OF PHOSPHORIC ACID SOLUTIONS.

(*Gm. per cent.=gm. of* H_3PO_4 *in* 100 *gm. of Solution.*)

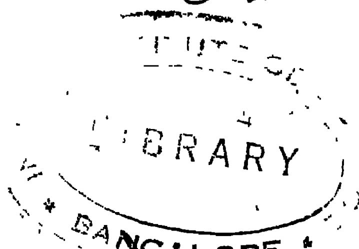
Gm. per cent.	S.G. $\frac{15° C.}{15° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{15° C.}$	Gm. per cent.	S.G. $\frac{15° C.}{15° C.}$
1	1·0054	21	1·1262	41	1·2731
2	1·0109	22	1·1329	42	1·2812
3	1·0164	23	1·1397	43	1·2894
4	1·0220	24	1·1465	44	1·2976
5	1·0276	25	1·1534	45	1·3059
6	1·0333	26	1·1604	46	1·3143
7	1·0390	27	1·1674	47	1·3227
8	1·0449	28	1·1745	48	1·3313
9	1·0508	29	1·1817	49	1·3399
10	1·0567	30	1·1889	50	1·3486
11	1·0627	31	1·1962	51	1·3573
12	1·0688	32	1·2036	52	1·3661
13	1·0749	33	1·2111	53	1·3750
14	1·0811	34	1·2186	54	1·3840
15	1·0874	35	1 2262	55	1·3931
16	1·0937	36	1·2338	56	1·4022
17	1·1001	37	1·2415	57	1·4114
18	1·1065	38	1·2493	58	1·4207
19	1·1130	39	1·2572	59	1·4301
20	1·1196	40	1·2651	60	1·4395

SPECIFIC GRAVITY AND REFRACTIVE INDEX OF GLYCEROL.

Glycerol per cent.	S.G. 15° C./15° C.	Refractive Index 15° C.	Glycerol per cent.	S.G. 15° C./15° C.	Refractive Index 15° C.
100	1·2653	1·4742	78	1·2074	1·4414
99	1·2628	1·4728	77	1·2046	1·4399
98	1·2602	1·4712	76	1·2018	1·4384
97	1·2577	1·4698	75	1·1990	1·4369
96	1·2552	1·4684	74	1·1962	1·4354
95	1·2526	1·4670	73	1·1934	1·4339
94	1·2501	1·4655	72	1·1906	1·4324
93	1·2476	1·4640	71	1·1878	1·4309
92	1·2451	1·4625	70	1·1850	1·4295
91	1·2425	1·4610	65	1·1711	1·4220
90	1·2400	1·4595	60	1·1570	1·4144
89	1·2373	1·4580	55	1·1430	1·4069
88	1·2346	1·4565	50	1·1290	1·3996
87	1·2319	1·4550	45	1·1155	1·3924
86	1·2292	1·4535	40	1·1020	1·3854
85	1·2265	1·4520	35	1·0885	1·3785
84	1·2238	1·4505	30	1·0750	1·3715
83	1·2211	1·4490	25	1·0620	1·3647
82	1·2184	1·4475	20	1·0490	1·3581
81	1·2157	1·4460	10	1·0245	1·3452
80	1·2130	1·4444	0	1·0000	1·3330
79	1·2102	1·4429			

APPARENT WEIGHT IN GM. OF 1000 ML. OF WATER IN AIR.

Temperature, ° C.	Weight of 1000 ml. Gm.	Temperature, ° C.	Weight of 1000 ml. Gm.
15	998·05	23	996·53
16	997·90	24	996·29
17	997·74	25	996·04
18	997·56	26	995·79
19	997·38	27	995·52
20	997·18	28	995·24
21	996·97	29	994·96
22	996·76	30	994·66



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